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INFLUENCE OF SOURCE TYPES AND SOURCE AREAS ON THE CONCENTRATIONS OF VOLATILE ORGANIC COMPOUNDS IN SOUTHERN FINLAND

JOHANNA PATOKOSKI

Division of Atmospheric Sciences

Department of Physics

Faculty of Science

University of Helsinki

Helsinki, Finland

Academic dissertation

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Author's Address:
Department of Physics
P.O.Box 64
FI-00014 University of Helsinki
johanna.patokoski@helsinki.fi

Supervisors:
University Lecturer Taina Ruuskanen, Ph.D.
Department of Physics and
Palmenia Centre of Continuining Education
P.O. Box 64
FI-00014 University of Helsinki

Prof. Janne Rinne, Ph.D.
Department of Geosciences and Geography and
Department of Physics and
Finnish Meteorological Institute
P.O.Box 64
FI-00014 University of Helsinki

Prof. Hannele Hakola, Ph.D.
Atmospheric Composition unit, Air Quality
Finnish Meteorological Institute
Erik Palménin aukio 1, 00560 Helsinki, Finland

Reviewers:
Docent Jorma Joutsensaari, Ph.D.
Department of Applied Physics
University of Eastern Finland
Kuopio, Finland

Professor Jyrki Mäkelä, Ph.D.
Department of Physics
Tampere University of Technology
Tampere, Finland

Opponent:
Senior researcher Steffen M. Noe, Ph.D.
Department of Plant Physiology
Estonian University of Life Sciences
EE-51014 Tartu, Estonia

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Influence of source types and source areas on the concentrations of volatile organic compounds in Southern Finland

Johanna Maria Patokoski

University of Helsinki, 2015

Abstract

Volatile organic compounds (VOCs) are known to be key players in the atmospheric processes. They are emitted both from natural and non-biogenic sources. Although the biogenic sources are generally dominant compared with the anthropogenic sources in some circumstances the anthropogenic emissions can dominate e.g. in densely populated areas or during pollution plumes. VOCs are ambient trace gases including a vast group of compounds. Some of the VOCs are very reactive, participating in atmospheric transformation processes e.g. secondary organic aerosol formation and growth. Some VOCs are also known to be harmful air pollutants for humans. Thus VOCs can have direct effects on air quality and secondary effects on climate.

In this thesis, the aim was to define sources of VOCs, determine influence of transport and transformation of trace gases and aerosols.

VOCs were measured mainly by a real time proton transfer reaction mass spectrometer. In addition, gas and liquid chromatography were used. The measurements were conducted at the rural SMEAR II and the urban background SMEAR III sites.

Concentrations of VOC were observed to have inter-annual, seasonal and diurnal variations due to meteorological factors, photochemistry and different sources. The anthropogenic influence was dominant in winter at both sites, while the biogenic influence with enhanced photochemical reactions increased in spring. The mixing and dilution effect also increased in spring and it led to decreased levels of volume mixing ratios (VMRs) in daytime especially in short-lived compounds. The VMRs of aromatic compounds were lower in spring than in winter due to lesser sources and enhanced photochemistry at both sites. At the urban background site there were more local sources than rural site and thus more variation of the diurnal patterns; higher VMRs of VOCs were observed. At both sites long-range transport was found to be an important source for long-lived VOCs. The source areas of long-lived VOCs were studied with trajectory analysis. Eastern Europe including West Russia was found to be major source area for all studied VOCs. In addition, some of them had specific source areas of their own related e.g. to their use in the solvent industry. During measurements there were two different forest fire episodes in Eastern Europe and a one-day prescribed biomass burning experiment. VMRs of VOCs related to burning were observed to increase during these pollution plumes. Atmospheric oxidation of BVOCs (biogenic VOCs) revealed that monoterpenes and their oxidation products by O_3 were limiting factors for nucleation particle growth. Study of total OH reactivity showed that there are a number of unmeasured biogenic compounds which may have effects on the local atmospheric chemical processes.

Keywords: variation of VOC concentrations, source analysis, long-range transport, forest fires, atmospheric chemistry

Abbreviations and chemical compounds

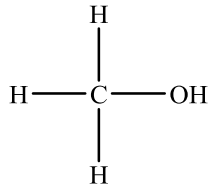
AVOC	anthropogenic volatile organic compound
BVOC	biogenic volatile organic compound
CO	carbon monoxide
CO_2	carbon dioxide
DNPH	dinitrophenyl hydrazine
ELVOC	extremely low volatility organic compound
H_2O	water
H_3O^+	hydronium ion
IVOC	intermediate volatility organic compound
LVOC	low volatility organic compound
M+1	protonated mass, notation for PTR-MS
MBO	methylbutenol
MEK	methyl ethyl ketone
MVK	methyl vinyl ketone
m/z	mass to charge ratio
NO_3	nitrate radical
NO	nitrogen oxide
NO_2	nitrogen dioxide
NO_3	nitrate radical
NO_x	oxides of nitrogen (NO+NO2)
O	molecular oxygen
O_2	oxygen
O_3	ozone
OH	hydroxyl radical
OR	monoterpene oxidation product
OVOC	oxygenated volatile organic compound

PAN	peroxyacetyl nitrate
PTR-MS	a proton transfer reaction mass spectrometer
ppb_v	parts per billion by volume
ppm_v	parts per million by volume
ppt_v	parts per trillion by volume
SMEAR	station for measuring forest ecosystem atmospheric interactions
SVOC	semi-volatile organic compound
$R^{\cdot}$	alkyl radical
$RO^{\cdot}$	alkoxy radical
$RO_2^{\cdot}$	alkyl peroxy radical
$ROONO_2$	peroxy nitrate
ROOH	peroxide
$RONO_2$	alkyl nitrate
VMR	volume mixing ratio is V_{VOC}/ V_{air} ,where V_{VOC} is volume of VOC and V_{air} is volume of air in which VOC is included
VOC	volatile organic compound
u*	friction velocity
z	height
z/u*	mixing time scale

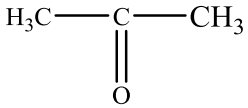
Key compounds and their structures

Oxygenated volatile organic compounds (OVOCs)

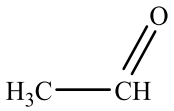
Methanol CH_3OH



Acetone CH_3COCH_3

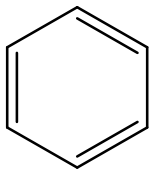


Acetaldehyde CH_3CHO

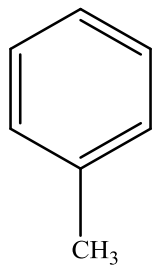


Anthropogenic volatile organic compounds (AVOCs)

Benzene C_6H_6

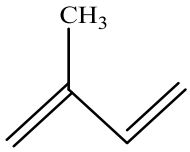


Toluene $C_6H_5CH_3$



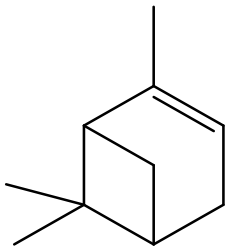
Biogenic volatile organic compounds (BVOCs)

Isoprene C_5H_8

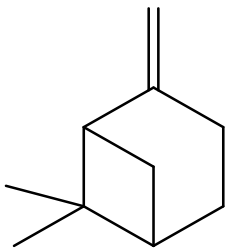


Monoterpenes with the general formula $C_{10}H_{16}$ e.g.

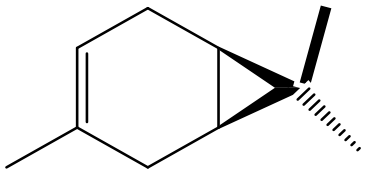
α-pinene



β-pinene



Δ^3-carene



Contents

List of publications

I. **Patokoski, J.,** Ruuskanen, T. M., Hellén, H., Taipale, R., Grönholm, T., Kajos, M. K., Petäjä, T., Hakola, H., Kulmala, M., Rinne, J., 2014**.** Winter to spring transition and diurnal variation of VOCs in Finland at an urban background site and a rural site. *Boreal Environment Research* 19, 79–103.

II. **Patokoski, J**., Ruuskanen, T.M., Kajos, M.K., Taipale, R., Rantala, P., Aalto, J., Ryyppö, T., Nieminen,T., Hakola, H., Rinne, J., 2015. Sources of long-lived atmospheric VOCs at the rural boreal forest site, SMEAR II. *Atmospheric Chemistry and Physics Discussions* 15, 14593-14641.

III. Yli-Juuti, T., Nieminen, T., Hirsikko, A., Aalto, P. P., Asmi, E., Hõrrak, U., Manninen, H. E., **Patokoski, J**., Dal Maso, M., Petajä, T., Rinne, J., Kulmala, M., Riipinen, I., 2011. Growth rates of nucleation mode particles in Hyytiälä during 2003-2009: variation with particle size, season, data analysis method and ambient conditions. *Atmospheric Chemistry and Physics* 11, 12865-12886.

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1. Introduction

The volatile organic compounds (VOCs) in the ambient air play an important role in atmospheric processes and also have primary and secondary effects (e.g. health effects of some VOCs and ozone formation) on air pollution (Koppmann, 2007 and references therein). Therefore, it is important to investigate the sources of VOCs, their transport from biosphere to the atmosphere and also the effect of the long-range transport on the concentrations of VOCs because of their impact on air quality and climate change studies.

In this thesis the focus is on organic trace gases whose volume mixing ratios (VMR) are at low levels varying from some ten parts per billion (10^{-9}, ppb_v) down to a few parts per trillion (10^{-12}, ppt_v). The abbreviation VOC includes a large variety of organic compounds with different structures and functional groups e.g. alkenes, amines, alcohols and carbonyls. VOCs are often defined as organic compounds having 15 or less carbon atoms in their structure, whose vapour pressure is over 10 Pa at 25°C and whose boiling point at atmospheric pressure is up to 260°C (Williams and Koppmann, 2007). VOCs are a diverse group of compounds varying from the strong-smelling monoterpenes released e.g. from forests (Kesselmeyer and Staudt, 1999) to harmful and even carcinogenic compounds such as the aromatic compounds, e.g., benzene and toluene (Kampa and Castanas, 2008; Muezzinoglu et al., 2001) released in traffic exhausts (Blake et al., 2009). As can be seen, they are emitted into the atmosphere from both natural and non-biogenic sources (Blake et al., 2009; Williams and Koppmann, 2007). Different VOCs can be classified according to their origin, i.e., as either biogenic VOCs (BVOCs) e.g. isoprene and the monoterpenes or anthropogenic VOCs (AVOCs) e.g. benzene. However, this classification is not always unambiguous. Some VOCs, e.g. methanol (CH_3OH), have both biogenic and anthropogenic sources (Jacob et al., 2005) and could be included in either BVOCs or AVOCs; but methanol can also be classified as an oxygenated VOC (OVOC).

Globally, total VOC emissions have been estimated to be about 1300 TgC/year (Guenther, 2002). The major part of these emissions (1150 TgC/year) comprises BVOCs emissions from vegetation and oceans (Fehsenfeld et al., 1992; Müller, 1992; Goldstein and Galbally, 2007). Major vegetation sources include forests with their diverse undergrowth, including shrubs, grasses and mosses (Steiner and Goldstein, 2007). Although the VOC emissions from oceans are known to be lower than those from terrestrial vegetation (Guenther et al., 1995), the oceans may be a significant source for some OVOCs, thus having an impact on the atmospheric processes in marine environments where other sources are sparse (Singh et al., 2000, 2001, 2004). AVOC emissions (including biomass burning) are estimated to be about an order of magnitude lower (185 TgC/year) than biogenic emissions. However, in certain areas or conditions, e.g., in densely-populated urban areas, during winters or in pollution plumes e.g. of forest fires, non-biogenic emissions can occasionally dominate (Simpson et al., 1999). In Europe, VOC emissions depend a lot on the area considered but also on the season. In northern areas, biogenic emissions dominate during summer but are

known to be low during winter, due to the cold environment and dormant vegetation; anthropogenic emissions are then dominant (Hakola et al., 2003). Globally, the main anthropogenic sources of VOCs are extraction, refining and the incomplete burning of fossil fuels (78 TgC/year), the evaporation of solvents related to the production of, e.g., paints, adhesives and pharmaceuticals (27 TgC/year) and biofuel combustion in heat and electrical power generation (30 TgC/year). Emissions from biomass burning are also an important source of VOCs, and are estimated to be 49 TgC/year (Reimann and Lewis, 2007 and references therein). The various different sources contributing to ambient VOC concentrations have been studied, e.g., with multivariate receptor models (Henry, 1997; Hellén et al., 2006, 2012). Hellén et al. (2006, 2012) observed several local sources of VOCs in an urban environment including traffic, wood combustion, city gas and gasoline evaporation. In addition to these local sources, regional and distant sources have also been observed to have a significant influence on measured VOC concentrations (Hellén et al., 2012; Ruuskanen et al., 2009). Using backward trajectories, the origins of these transported air masses can be studied and potential source areas for the trace gases can be identified (Draxler and Hess, 1998; Riuttanen et al., 2013**)**. The sources affecting the observed concentrations of VOCs can vary from stationary areal ones such as the large boreal vegetation zone, to smaller local point sources, such as power plants. The vertical profiles of VOCs may have a large variation due to nearby sources. However, in this study the sources are assumed to be further away from the site and the measured VOCs to be well-mixed in the boundary layer.

After being released into the atmosphere from their various different sources, VOCs can react with atmospheric oxidants or undergo photolysis. Deposition is also a sink for VOCs. The main atmospheric oxidants for VOCs are the hydroxyl (OH) and nitrate (NO_3) radicals and ozone (O_3) (Atkinson and Arey, 2003). The reactivity towards oxidants, the photolysis rates and the lifetimes of VOCs vary between compounds from lifetimes of a few minutes to about an hour for BVOCs e.g. β-caryophyllene and α-pinene, to lifetimes of several days for e.g. benzene or some OVOCs (Williams and Koppmann, 2007; Kessermeier and Staudt, 1999). The temporal and horizontal spatial scales of some short- and long-lived VOCs are presented in Figure 1. The lifetimes of short-lived VOCs are estimated to be some hours and the lifetimes of long-lived VOCs more than one day. The long-lived VOCs are oxidized relatively slowly and thus they can be transported over long distances. The very reactive short-lived BVOCs are oxidized quickly and this occurs locally. BVOCs are known to participate in the production and destruction processes of tropospheric ozone (Chameides et al., 1992; Vogel et al., 1995; Roselle et al., 1997) and some of their oxidation products are found to undergo gas-to-particle conversions (Tunved et al., 2006; Kulmala et al., 2004).

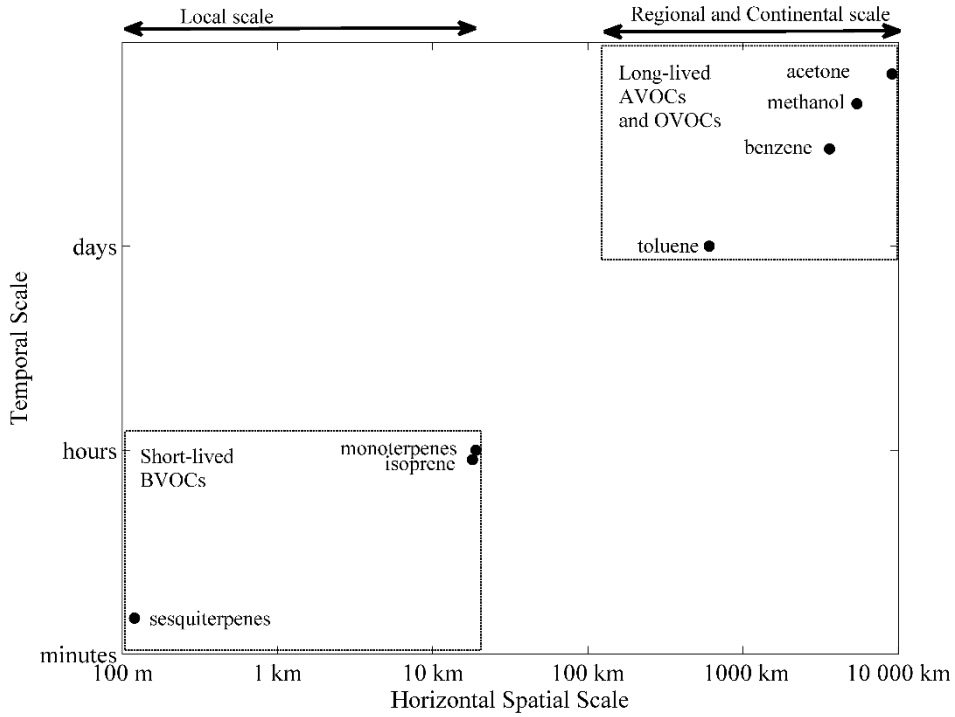

Figure 1. Temporal and horizontal spatial scales of the VOCs with short and long lifetimes. The temporal scale is determined based on the reactivity of the VOCs. The horizontal spatial scale is determined using different horizontal wind velocities (v) and lifetimes (τ) for different VOCs: for sesquiterpenes v ~ 1m/s and τ ~ 2 min, for isoprene and monoterpenes v ~ 4 m/s and τ ~ 1 h; for long-lived VOCs v ~ 7 m/s and τ ~ 1 d for toluene, τ ~ 6 d for benzene, τ ~ 9 d methanol and τ ~ 15 d acetone.

The vapour pressure of the oxidation products of VOCs have been found to be lower than that of the original compounds (Figure 2) due to an addition of functional groups (oxygen including groups) (Pandis et al., 1992). The oxidized compounds of VOCs have higher polarity and thus lower volatility than their precursor compounds (Pandis et al., 1992; Goldstein and Galbally, 2007). These low and extremely low volatility oxidation products of VOCs have been observed in several studies (e.g. Robinson et al, 2007; Donahue et al., 2009; Ehn et al., 2014; Kulmala et al., 2004; Riipinen et al., 2011) to be able to condense on surfaces, and thus participate in secondary organic aerosol (SOA) formation and particle growth processes. In addition to the volatility of the oxidation products, BVOCs' ability to participate in SOA formation is dependent on the chemical reactivity and abundance of BVOCs in the atmosphere (Seinfeld and Pandis, 1998). Globally, a remarkable amount of organic particulate matter is derived from SOA formation and only a minor part from different primary particle emissions (Kanakidou et al., 2005; Hallquist et al., 2009). The importance of BVOCs as contributors in secondary organic aerosol (SOA) formation has been shown by e.g. Went (1960); Andreae and Crutzen (1997); Hoffmann et al. (1997);

Pandis et al. (1991, 1992); Kroll and Seinfeld (2008). They have been estimated to account for 20-90 % of SOA formation in the lower troposphere (Kanakidou et al., 2005). Although the more reactive BVOCs usually dominate the SOA and ozone formation, the less reactive AVOCs and OVOCs can also participate in these processes, for example in urban environments (Kanakidou et al., 2005; Hallquist et al., 2009; Hoyle et al. 2011; Odum et al., 1997; Ziemann and Atkinson, 2012).

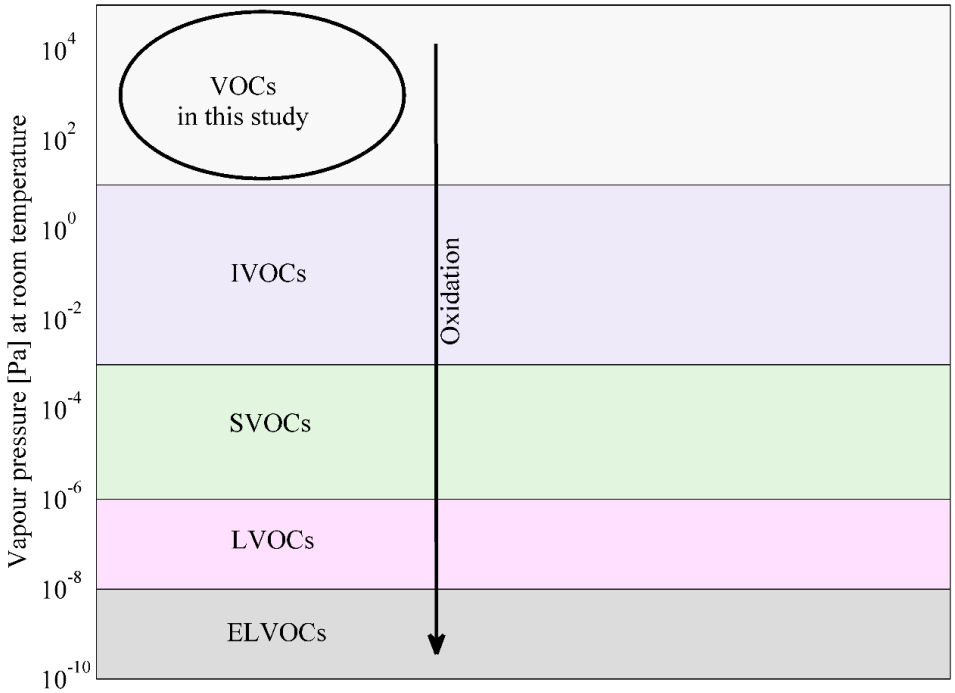

Figure 2. Volatility classes for VOCs based on vapour pressures [Pa] at room temperature. VOCs > 10 Pa, intermediate volatility organic compounds (IVOCs) 10^{-3} Pa-10 Pa, semi-volatile organic compounds (SVOCs) 10^{-6}-10^{-3} Pa, low volatility organic compounds (LVOCs) 10^{-8}-10^{-6} and extremely low volatility organic compounds (ELVOCs) < 10^{-8} Pa (Goldstein and Galbally, 2007; Donahue et al., 2012; Donahue et al., 2009; Ehn et al., 2014).

The primary oxidants of ambient VOCs are known to vary between compounds (Atkinson and Arey, 2003). However, the OH radicals are known to be the major oxidant for many VOCs (Atkinson, 1989, 1994; DeMore et al., 1997). Due to the ability of the OH radicals to degrade VOCs they are called “atmospheric detergents” (Lelieveld et al., 2008). Because VOC oxidation reactions are a sink for OH radicals, they may have an effect on the oxidative and cleaning capacity of the atmosphere (Lelieveld et al., 2008). Estimating the reactive trace gas budget correctly is thus important because reactive trace gases such as BVOCs

compete with methane (CH_4) for OH. The decrease in oxidative capacity may lead to an increase in CH_4, which is a strong greenhouse gas, thus having an effect on the climate (Lelieveld et al., 2004). The OH reactive trace gas budget has been estimated in several campaigns by measuring the total OH reactivity, e.g., in a mixed transition forest (Di Carlo et al., 2004), the tropics (Sinha et al., 2008), urban environments (Dolgorouky et al., 2012; Sinha et al., 2008) and in boreal forest (Sinha et al., 2010; Nölscher et al., 2012) and comparing it to the calculated OH reactivity. A difference between the measured and calculated OH reactivity, i.e. a missing OH reactivity, has been observed. The ratio of the missing part to the total OH reactivity has been observed to vary, depending on the types of sources of VOCs (Dolgorouky et al., 2012; Nölscher et al., 2012). For example, sites with biogenic emissions (Sinha et al., 2010; DiCarlo et al., 2004) differ from those affected by long-range transported VOC emissions including OVOCs of anthropogenic origin (Dolgorouky et al., 2012). It should be remembered, too, that the unknown reactive compounds contributing to the missing OH reactivity may have an effect on the formation of secondary pollution products (Mogensen et al., 2011).

VOCs have effects on human health, air quality and climate. In addition to the secondary compounds several compounds in the ambient air, including some of the VOCs, are known to be harmful to humans, e.g., by affecting the respiratory tract (Kampa and Castanas, 2008). The European Union has therefore set annual limit values for harmful air pollutants. For example the annual mean limit value for benzene, which is a carcinogenic compound, is 1.6 ppb_v (EU, 2000). VOCs also have secondary effects on human health by participating in the formation of particles and ozone, which are also known to be harmful to human health (WHO, 2003). From a climate point of view, the VOCs can have several indirect impacts through influencing the concentrations of greenhouse gases, e.g., tropospheric ozone or methane, SOA formation, participating in particle growth processes and the formation of climate-relevant cloud condensation nuclei (CCN), thus possibly modifying the cloud albedo (Tunved et al., 2006; Novakov and Penner, 1993). The climate change will increase temperatures and cause other changes e.g. in precipitation (IPCC, 2007) and thus affect the future emissions of VOCs leading to possible changes in SOA formation and radiative balance. Although the BVOCs emissions will change in the future, the results are contradictory. Rinne et al. (2009) concluded that the changes in precipitation and temperature will also lead to a change in vegetation that may reduce monoterpene emissions and increase isoprene emissions. In other studies the emissions of monoterpenes were assumed to increase because of enhanced photosynthesis and temperature (Räisänen et al., 2008a; Ashworth et al., 2013) and the emissions of isoprene were also observed to increase at first due to increased temperature (Monson and Fall, 1989; Pètron et al., 2001). The increased CO_2 concentration has however been observed to inhibit the emissions of isoprene (Arneth et al., 2007; Ashworth et al., 2013; Rosenstiel et al., 2003). Also the emissions of AVOCs are estimated to change in the future. The emissions of AVOCs will increase due to the population and economic growth according to Williams and Koppmann (2007).

However, it has been reported that AVOC emissions will decrease due to technical advances and emission regulations (Millstein and Harley, 2009; Steiner et al., 2006).

As can be seen the VOCs evidently have a role in many different atmospheric processes. Thus their concentrations and behaviour have been studied in various different environments, including several forest types, e.g. tropical rainforests, temperate coniferous forests and northern boreal forests; other environments, from rural and remote areas to densely-populated cities by e.g. Warneke et al. (2001); Crutzen et al. (2000); Müller et al. (2006); Hakola et al. (2012); Hellén et al. (2004, 2006, 2012); Rinne et al. (2005); Ruuskanen et al. (2009); Lappalainen et al. (2009); Langford et al. (2010); Kato et al. (2004); Holzinger et al. (2002). The concentrations of VOCs were observed to have temporal and spatial variations (as e.g. by Hakola et al., 2012; Ruuskanen et al., 2009; Filella and Peñuelas, 2006; Rinne et al., 2005). The variations in VOC concentrations and their seasonal and diurnal patterns often result from several factors, e.g., the reactivity of the compounds, different sources, transportation, the location of the site and meteorology (Reimann and Lewis, 2007). In some circumstances, the concentrations may vary considerably: this is so, for example in northern Europe between winter and spring due to the increase in biogenic and photochemical activity (Hakola et al., 2006). The investigation of the VOC concentrations and their variations is important because the increase in biogenic emissions and photochemical activity have also been proposed to be one of the important feedback mechanisms between the biosphere and the atmosphere (Dal Maso et al., 2009; Kulmala et al., 2004).

To measure VOC concentrations and their variations, different measurement techniques are needed. Formerly VOCs were mainly measured using on-site sampling techniques with off-site analysis. Samples were collected into adsorbents contained in tubes, cartridges or canisters, which were later analyzed in the laboratory using, for example gas or liquid chromatography (GC/LC). However, these methods are quite laborious and the time resolution of the resulting time series was low. This leads to an inability to measure especially very rapid changes in concentrations. In the early 1990's a new method, proton transfer reaction mass spectrometry, was developed for atmospheric VOC measurements (Lindinger et al., 1998a, b). The advantage of the proton transfer reaction mass spectrometer (PTR-MS) is its fast response, resulting high time resolution and the ability to measure in real-time. Although the gas chromatography mass spectrometer (GC-MS) has a lower time resolution than PTR-MS, an advantage of GC-MS is its better ability to separate specific compounds, e.g., different monoterpenes. Both of these methods are widely used in ambient measurements (e.g. de Gouw et al., 2003; de Gouw and Warneke, 2007; Hellén et al., 2004, 2006, 2012; Hakola et al., 2000, 2006, 2012; Noe et al., 2012; Rinne et al., 2007; Ruuskanen et al., 2009) and they complement each other.

In this thesis, the VMRs of VOCs were mostly measured with PTR-MS supported by GC/LC-MS. The concentrations of VOCs, their variations due to different sources, source areas, pollution episodes, meteorology and atmospheric chemistry were studied, as were also

their exchange between the biosphere and the atmosphere. Sources of VOCs and their variation were studied using data from different seasons and sites using a multivariate receptor model. The source areas were investigated using continuous long-term time series of trace gases and backward trajectories. As was previously mentioned, on a global scale the major part of VOC emissions has a biogenic origin and only 10 % originates from anthropogenic sources. In this thesis, the **general aim** was to define the sources of VOCs, as well as to determine the influence of transport and transformation on the trace gases and aerosols observed in Southern Finland. The specific aims of this study were

- to define the sources of trace gases for Southern Finland specifically to determine the biogenic versus the anthropogenic influence (**papers I and II**)
- to determine the sources which have effect on the VOC VMRs and their inter-annual, seasonal and diurnal variability at the rural and urban background sites during the transition from winter to spring (**papers I and V**)
- to evaluate temporally (forest fires) or spatially (industrial areas) defined source areas which have effect on the VOC VMRs (**papers II and VI**)
- to study the influence of atmospheric chemistry on VOCs especially
    - the effect of monoterpenes' oxidation products on nucleation mode particle growth (**paper III**)
    - the influence of VOCs on the OH oxidative capacity of the atmosphere (**paper IV**)

2. Atmospheric chemistry

The main atmospheric oxidants of VOCs are the OH radicals, O_3 and the NO_3 radicals. In addition to oxidation with radicals, some of the VOCs are transformed in the atmosphere by photolysis (at wavelengths > 290 nm). The OH radical is known to be the most important oxidant for several VOCs in the troposphere (Atkinson, 1989, 1994; DeMore et al., 1997; Atkinson et al., 1997). OH radicals are mainly produced by the photolysis of ozone in the presence of water vapour (Levy, 1971).

$$O_3 + h\nu \rightarrow O_2 + O \quad (1)$$

$$O + H_2O \rightarrow 2\ OH \quad (2)$$

Thus VOCs react with OH radicals mainly during daylight hours. Ozone is formed from the photo-dissociation reaction of NO_2 in the presence of atmospheric oxygen, thus:

$$NO_2 + h\nu \rightarrow NO + O \quad (3)$$

$$O + O_2 \rightarrow O_3 \quad (4)$$

NO_3 radicals are mainly formed in the reaction of NO_2 with O_3

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (5)$$

During the daytime NO_3 is decomposed back to NO_2 or NO by photolysis (Wayne et al., 1991); VOCs thus react with NO_3 mainly during evenings and nights.

In the atmosphere, VOCs react with oxidants mainly by addition and abstraction mechanisms. Figure 3 shows the general reaction scheme of BVOC oxidation (Atkinson and Arey, 2003). In the addition mechanism, O_3, OH and NO_3 radicals are added to the BVOCs' carbon-carbon double bond. In the abstraction mechanism an H atom is removed from the hydrogen–carbon bond by OH or NO_3. The primary product of an oxidation reaction via either the addition or the abstraction mechanism is an alkyl radical ($R^{\cdot}$). This is a reactive intermediate, which readily reacts with O_2 forming an alkyl peroxy radical ($RO_2^{\cdot}$). The alkyl peroxy radical ($RO_2^{\cdot}$) can react with NO, NO_2, HO_2 or another alkyl peroxy. An alkyl peroxy reacts 1) with NO_2 forming peroxy nitrates ($ROONO_2$), which can be reservoir compounds

for NO_x because they are stable in atmospheric conditions and can thus be transported for long distances or 2) with HO_2 forming peroxides (ROOH), which is a sink reaction for radicals. ROOH can itself react further with OH, regenerate OH via photolysis or become removed via dry or wet deposition. In an alkyl peroxy's reaction with NO or NO_2 ozone can be produced. The reaction direction is dependent on the NO mixing ratio. If the NO mixing ratio is low, the favoured reaction direction is towards HO_2/RO_2, radicals are removed and the formation of ozone is inhibited. In reaction with two $RO_2^{\cdot}$ radicals, OVOCs such as alcohols, ketones and aldehydes are produced. If a lot of NO is available, as in polluted areas, peroxy radicals are inclined to react with NO and NO_2. $RO_2^{\cdot}$ and NO can together produce alkyl nitrate ($RONO_2$) or the alkoxy radical ($RO^{\cdot}$). Alkyl nitrate is known to be more stable, and NO_x can be removed from the reaction cycle. If the alkoxy radical is produced, a variety of products can be isomerized or decomposed, resulting in NO_2 formation; also, ozone formation can further be initiated (Atkinson and Arey, 2003; Steiner and Goldstein, 2007).

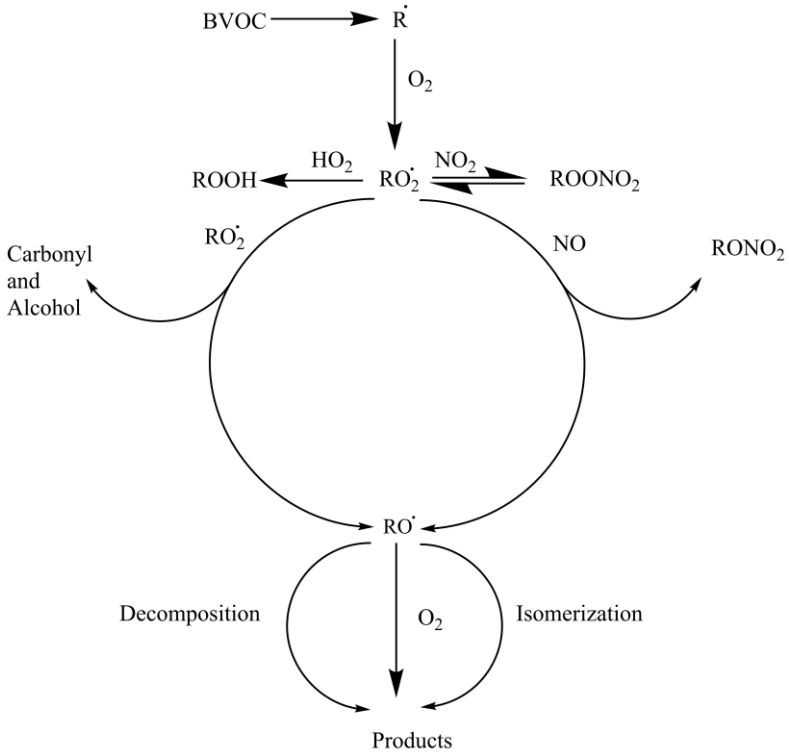

Figure 3. General reaction scheme of BVOC oxidation, adapted from Atkinson and Arey (2003).

Aromatic compounds are also oxidized by OH and NO_3 radicals. Both the OH addition and the abstraction of H-atoms are possible reactions. However, the addition of OH to the aromatic ring is the main decomposition route (Atkinson, 2000), after which, with the addition of molecular oxygen, a cyclic hydroxy peroxy radical is formed. The opening of the

ring structure produces epoxy compounds, together with different saturated and unsaturated dicarbonyl radicals and finally methylglyoxal. The H-atom abstraction from the alkyl substitute group forms aromatic aldehyde, e.g., the end-product in the case of toluene is bentsaldehyde (Reimann and Lewis, 2007).

The OVOCs are similarly oxidized with OH and NO_3, but some of them include photoactive groups, and are thus degraded via photolysis (Atkinson, 2000). In photolysis free radicals and stable products are formed. For example in the photolysis of acetaldehyde, methyl and acyl radicals as well as methane and carbon monoxide are formed (Finlayson-Pitts and Pitts, 2000). The addition of O_3 is also possible for unsaturated OVOCs. An important degradation reaction for OVOCs is hydrogen abstraction by OH radicals in the presence of O_2 in which peroxy radicals are formed (Reimann and Lewis, 2007). If there is enough NO_2 available, the peroxy radicals are formed from acetaldehyde. They are precursors for peroxyacetyl nitrates (PANs) which are related to air quality issues: due to their stability in cold environments, they can transport NO_x from urbanized and industrialized areas into rural areas. Thus they may have an effect on the tropospheric ozone production which in rural areas is known to be NO_x limited (Sillmann, 1999).

3. Methods

3.1. Measurements

VOCs are a diverse group of compounds with varying polarity and volatility. Their mixing ratios in the atmosphere are also usually very low (Blake et al., 2009). Thus different methods, both off and online, are needed to measure and analyze them (Janson et al., 1992; Fraser et al., 1997; de Gouw and Warneke, 2007; Noe et al., 2012; Hakola et al., 2012; Rinne et al., 2007; Ruuskanen et al., 2005). The most widely used method is to collect the VOCs into adsorbents, canisters or cartridges and make analysis later offline in the laboratory using gas chromatography mass spectrometry (Grosjean et al., 1998; Na and Kim, 2001; Sauvage et al., 2009; Hakola et al., 2000; Hellén et al., 2004). Nowadays the use of automated measurements such as an online GC and chemical ionization methods has become more common (Lewis et al., 1997; Lindinger et al., 1998 a,b). In this thesis, VOCs were measured mainly with a quadrupole PTR-MS (Ionicon Analytik GmbH, Lindinger et al., 1998a, b) (**papers I-III**, **VI**) and complemented with GC/LC-MS analysis (**papers IV**, **V**).

3.1.1. The proton transfer reaction mass spectrometer (PTR-MS) and sampling

PTR-MS is a real-time instrument which was originally developed for atmospheric measurements (Blake et al., 2009). Similar to GC-MS, which was used in **paper V**, it is widely used in ambient VOC measurements (e.g Lindinger et al., 1998a, b; Hayward et al., 2002; Amman et al., 2004; de Gouw and Warneke, 2007; Rinne et al., 2007; Blake et al., 2009; Ruuskanen et al., 2009; Seco et al., 2013). In the PTR-MS, the hydronium ion (H_3O^+) is used as the primary reactant ion. VOCs having a larger proton affinity than water (H_2O) will readily react with H_3O^+ (Lindinger et al., 1998a, b), making this method appropriate for atmospheric VOC measurements. The usage of a soft ionization method in PTR-MS results in many compounds hardly being fragmented at all (Tani et al., 2003). The reactant ion is formed in an ion source from water vapour by hollow cathode discharge. The ambient VOCs react with the hydronium ion in a drift tube. After passing through the drift tube, the reactant and the product ions (M+1) are mass filtered with a quadrupole mass spectrometer and detected with a secondary electron multiplier (SEM). The VOCs are identified based on their protonated masses or more exactly mass-to-charge (m/z) ratio. We assume z = 1 and e.g. for methanol m/z = 33. The advantage of the PTR-MS as compared to GC-MS is its ability to measure rapidly (response time 0.1-10 s) and in real-time with high sensitivity (varying from 10-100 ppt_v for suite of VOCs) without pre-treatment of the samples (de Gouw et al., 2003; Warneke et al., 2003; Blake et al., 2009). This is important in atmospheric VOC measurements, in which measured VMRs are relatively low. Although GC-MS has been considered the accepted reference standard for the measurement of atmospheric trace gases and can achieve very high sensitives varying from few ppt_v to tens of ppt_v for some of VOCs, it has suffered from a low time resolution and the laborious analysis needed (Ellis, 2014). In

paper V VOCs were analyzed with an offline GC-MS. However, with the offline GC-MS it was only possible to obtain detailed snapshots. With the offline method, rapid changes in atmospheric conditions could not be followed (Blake et al., 2009). VOCs measurements with online GC-MS instruments have recently became more common. Thus longer measurement campaigns can nowadays be conducted more easily than before. Although the time resolution has improved, the GC-MS sampling still takes several minutes at least (plus analysis time, if it is an online GC). With the PTR-MS, quickly-changing atmospheric conditions can thus be measured better than with an online GC-MS. However, the disadvantage of PTR-MS is that it measures the sum of all compounds having the same mass, and is therefore not able to separate different compounds when the have same mass, e.g., monoterpenes (Warneke et al., 2003), as GC-MS can. Thus several comparison measurements between PTR-MS and GC-MS have been conducted to enhance the identification of compounds, e.g., by Warneke et al. (2001, 2003); de Gouw et al. (2003); Kuster et al. (2004); Rogers et al. (2006); Ruuskanen et al. (2005); Kajos et al. (2015).

To ensure reliable measurements it is important to calibrate the PTR-MS regularly. During these measurements, the PTR-MS was calibrated once a week or biweekly with a VOC calibration mixture. Taipale et al., 2008 have presented the calibration procedure and the VMR calculation methodology. Related to this thesis, VOCs were measured at two different SMEAR (Station for Measuring Ecosystem-Atmosphere Relations) sites: the rural SMEAR II, at Hyytiälä, and the urban background SMEAR III, in Helsinki; these are described later in chapter 3.1.3. The measurement set-up at SMEAR II during the years 2006-2009 has been earlier described in detail by Ruuskanen (2009) and Taipale (2011). In spring 2010, the measurement place and the sampling protocol changed, the PTR-MS being transported to another measurement hut. The sampling line was also moved about 20 m to a mast and thereafter VOC VMR data were obtained at six different heights (from 4.2 m to 67 m). PTR-MS measurements at SMEAR II are made at heights of 14.6 m (**paper I**) and 22 m and 33.6 m (**paper II**). At SMEAR III, ambient VOC VMRs were continuously measured at the height of the fourth floor of the University of Helsinki building above a small street. A detailed description of flows and length of tubings in SMEAR III can be found in **paper I**.

3.1.2. Adsorbent samples

Two different types of adsorbent samples were used to determine ambient air VOC concentrations in this thesis. In sampling, stainless steel tubes, filled with Tenax-TA and Carbopack-B, were used. The analysis procedures for GC-MS measurements used in this study are well-documented by Hakola et al. (2003, 2006). Tenax –TA and Carbopack adsorbents were used in the measurements utilized in **papers IV** and **V**. In **paper V** they are used to define long-term monoterpene variations. In **paper IV** they were used as additional VOC measurements to estimate the total oxidative capacity of VOCs in a boreal environment. Carbonyl compounds in ambient air were sampled using DNPH (2, 4-

dinitrophenyl hydrazine)-coated C-18 cartridges. The analysis of carbonyl compounds is described in detail by Hellén et al. (2004).

3.1.3.Measurement sites: SMEAR II and SMEAR III

The measurements included in this thesis were conducted at two different sites in Southern Finland. The geographical locations of the measurement sites are presented in Figure 4. The measurements related to **paper I** were conducted at both SMEAR II and SMEAR III, while the measurements for **papers II-VI** were conducted at SMEAR II only. The measurement periods are presented in Figure 5.

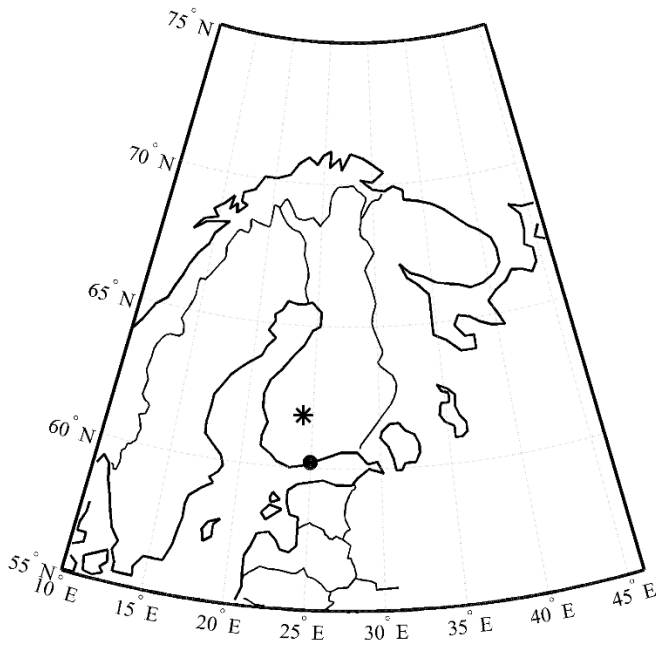

Figure 4. Map of the measurement sites. The black circle is the urban background site SMEAR III in Helsinki and black star is the rural site SMEAR II at Hyytiälä (**paper I**).

SMEAR II (Station for measuring Ecosystem-Atmosphere Relations II) is a rural station located at Hyytiälä, Southern Finland (61°51´N, 24°17´E, 180 m a.s.l.) where continuous long-term measurements of trace gases, aerosol particles and micrometeorology are carried out (Vesala et al., 1998). The station is located 190 kilometres from Helsinki and 50 kilometres from Tampere. Tampere, with a population of about 200 000, is the largest city near SMEAR II. The regional surroundings of the site are sparsely populated. However, there are two sawmills and a pellet factory at Korkeakoski, which is about 6 kilometres south-east of the site (Liao et al., 2011). The homogenous forest surrounding the station is

dominated by Scots pine (*Pinus sylvestris*) sown in 1962. There is also some Norway spruce (*Picea abies*), aspen (*Populus tremula*) and birch (*Betula sp.*) (Hari and Kulmala, 2005). Around the measurement tower the canopy height is around 16 metres. The station is described in detail by Hari and Kulmala (2005).

SMEAR III (Station for Measuring Ecosystem-Atmosphere Relations III) is an urban background measurement station in Helsinki, Southern Finland (60°12´N, 24°58´E, 26 m a.s.l.). Similar to SMEAR II, trace gases, aerosol particles and urban micrometeorology are also studied at SMEAR III (Järvi et al., 2009). The total population of the Helsinki metropolitan area (Helsinki, Espoo, Vantaa and Kauniainen) is about one million. The station is located five kilometres north-east of the centre of Helsinki. The surroundings of the station are heterogeneous, comprising both vegetated areas and roads. The nearest major road is 150 m from the SMEAR III measurement tower, and traffic rates are monitored at a distance of 2.5 km by the Helsinki City Planning Department (Järvi et al., 2009). Typical vegetation surrounding the station is park-like, with a very complex composition, including planted tree species as well as the University botanical garden and an allotment garden area (Vesala et al., 2008). However, trees in the immediate vicinity of SMEAR III are mainly Birch (*Betula* sp.), Norway maple (*Acer platanoides*), aspen (*Populus tremula*), goat willow (*Salix caprea*) and bird cherry (*Prunus padus*). The station and its measurements are described in detail in Vesala et al. (2008) and Järvi et al. (2009).

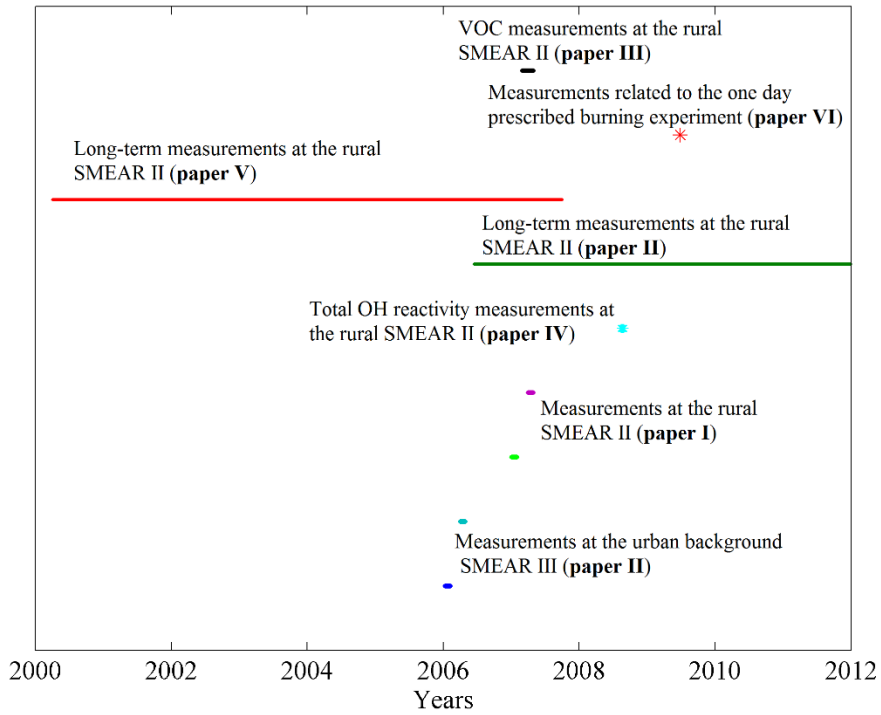

Figure 5. Measurements related to this thesis at SMEAR II and SMEAR III.

3.2. Data analysis

3.2.1. The multivariate receptor model Unmix 6.0

Various multivariate receptor methods, such as Unmix (Henry, 1997; Hellén et al., 2003), chemical mass balance (Hellén et al., 2006, 2003; Fujita et al., 1994; Vega et al., 2000), and principal component analysis (Edwards et al., 2001; Wang and Du, 2000) are used in the atmospheric sciences to determine the sources profiles of ambient trace gases and particles. With the help of the measured ambient concentrations, the receptor model attempts to discover which sources can explain these observations (Vallero, 2008). In the Unmix model only the measured ambient concentrations at receptor sites are used while in the chemical mass balance model both the emission profiles of sources and ambient concentrations are used.

The receptor models are based on the mass balance equation

$$C_{ij} = \sum_{k=1}^{N} a_{ik} S_{jk}\,, i = 1, \ldots., m, k = 1, \ldots., n \qquad (6)$$

where

C_{ij} is the observed concentration of species i in sample j, a_{ik}, is the fraction of species i in source k (k=1,….,N) (N is the number of sources) and S_{kj} is the total amount of material from source k in the sample. In this model it has been assumed that there are no loss processes of the elements between source and receptor.

In this thesis, the EPA Unmix 6.0 multivariate receptor model was used to study source compositions and contributions. This model has been developed by Ronald Henry at the University of Southern California. The fundamentals of Unmix are described by Henry (1997, 2002, 2007). A basic question of multivariate receptor models is how to determine the optimal number of sources, the source fingerprints and their contributions from the ambient air VOC measurement data alone. Some additional constraints can be brought in by the user to enable the achievement of a unique solution. In Unmix, the composition and contribution of the sources must be non-negative. In addition to this, Unmix searches for times when the data indicates that the contribution of one of the sources is either missing completely or its contribution is minor. The application of Unmix for VOC data in combination with data from chromatographic methods in Helsinki is described in Hellén et al. (2003). Unmix calculates some statistical parameters which can be used to evaluate the performance of the model. According to the model recommendations, the regression of each of the species explained by the sources (R^2) should exceed 0.8 while the signal-to-noise ratio should exceed 2. In this thesis, Unmix was employed in **papers I** and **II**.

3.2.2. Trajectory analysis

Trajectory analysis is a commonly-used tool to investigate the origins of air masses. Trajectories are shown to be applicable for depicting the long-distance transportation of atmospheric compounds from the sources to the receptor site (e.g. Draxler and Hess, 1998; Riuttanen et al., 2013; Sogacheva et al., 2005). Using trajectory analysis, the source areas of atmospheric compounds can be defined and also their influence on the measured concentrations at a receptor site can be estimated (Stohl 1996; Stohl and Seibert, 1998).

In this thesis, HYSPLIT 4 (HYbrit Single Particle Lagrangian Integrated Trajectory) backward air mass trajectories were used (Draxler and Hess, 1998) (**paper II**). At SMEAR II the arrival height of the calculated trajectories was 100 m above ground level, thus representing air masses arriving in the surface layer, in which the VOC VMR measurements were made. Backward trajectories of 96 hours (4 days) were calculated for every hour covering the years 2006-2011. For the purposes of the trajectory analysis, the VOC VMR data were interpolated using a Piecewise Cubic Hermite Interpolating Polynomial (PCHIP) to cover every hour and thus to match the trajectory data. Each time VOC VMR measured data were available at SMEAR II, they were associated with a trajectory arriving at the site at the same time. The path of the back trajectories was defined with a 1°x1° spatial resolution. The VMRs of trace gases were assumed to stay constant during the whole transport time. The grid cells which the trajectories traversed prior to the observation of high VMR values at SMEAR II were associated with high values in the source field. The trajectory analysis was restricted to the area between 50°N and 75°N in latitude, 12°E and 50°E in longitude. For reasons of statistical significance, at least 25 trajectories had to cross a grid cell, i.e., grid cells with less than 25 traverses were excluded from the analysis. Finally, all the VOC VMRs in each grid cell were averaged to generate the VOC source field (Stohl et al., 1995; Stohl and Seibert, 1998).

3.2.3. Lifetime calculations

In **papers I** and **II** the total atmospheric lifetimes of VOCs (τ) towards atmospheric oxidants (O_3, OH, NO_3) and photolysis were estimated. The lifetime is the time elapsed for 36.8 % (1/e) of the initial concentration of compound to be left in the atmosphere (Steiner and Goldstein, 2007). Lifetimes were calculated for selected compounds in winter, spring and summer for SMEAR II and in winter and spring for SMEAR III. The reaction rate coefficient for monoterpenes towards ozone and the hydroxyl radical were calculated using weighted averages of the reaction rate constants of the individual monoterpenes typical for SMEAR II, according to Hakola et al. (2003). In photolysis calculations two different approaches were used. In **paper I**, photolysis rates in winter were scaled using measured global radiation values from photolysis rates which Hellén et al. (2004), had calculated for the spring. In **paper II** the photolysis rates of selected compounds for winter and summer were calculated similarly to Hellén et al. (2004). The total lifetime τ was calculated using the equation

$$\tau = (k_{OH}[OH] \quad + k_{O_3}[O_3] \quad + k_{NO3}[NO_3] \quad + photolysis)^{-1} \qquad (7)$$

where

k_{OH} is the reaction rate coefficient for the VOC towards the hydroxyl radical, k_{O_3} is the reaction rate coefficient for the VOC towards ozone, and k_{NO_3} is the reaction rate coefficient for the VOCs towards NO_3.

3.2.4.Monoterpenes' oxidation production rate calculations

In **paper III**, factors having an impact on the growth rates of nucleation mode particles were studied. Several studies have shown that organic compounds, e.g. ELVOCs, are good candidates for participating in nucleation and particle growth (Tunved et al., 2006; Ehn et al., 2014; Riipinen et al., 2011). The production rates for monoterpene oxidation products were therefore calculated and correlated with the growth rates of nucleation mode particles. The oxidants which were used in these calculations were the hydroxyl radical and ozone. Nitrate radical was not included, because **paper III** was concerned with investigating nucleation mode growth rates, and the nucleation mode is mainly present in daytime. Oxidation production rates are calculated using

$$\frac{d[OR]_{OH}}{dt} = k_{OH}[OH][MT] \qquad (8)$$

$$\frac{d[OR]_{O3}}{dt} = k_{O3}[O_3][MT] \qquad (9)$$

where, k_{OH} is the reaction rate coefficient for the VOC towards the hydroxyl radical, $d[OR]_{OH}/dt$ is the formation rate of the monoterpene oxidation product in OH oxidation, [OH] is the measured hydroxyl radical concentration, [MT] is the measured sum concentration of monoterpenes, k_{O_3} is the reaction rate coefficient for the VOC towards ozone, $d[OR]_{O3}/dt$ is the formation rate of the monoterpene oxidation product in ozone oxidation, and $[O_3]$ is the measured ozone concentration.

Monoterpenes were used in these calculations because, in **papers I** and **II**, monoterpenes were observed to be one of the important BVOCs at SMEAR II.

4. Results and discussion

4.1. Lifetimes of VOCs and the primary oxidants for VOCs

The reaction rate coefficients k_{OH}, k_{O3}, k_{NO3}, photolysis rates and calculated atmospheric lifetimes for winter, spring and summer are listed in Tables 1, 2 and 3.

Table 1. Reaction rate coefficients (k_{OH}, k_{O3}, k_{NO3}) and photolysis rates for the measured VOCs (**papers I and II**).

	k_{OH}	k_{O3}	k_{NO3}	$k_{photolysis}$	$k_{photolysis}$	$k_{photolysis}$
	[$cm^3molec^{-1}s^{-1}$]	[$cm^3molec^{-1}s^{-1}$]	[$cm^3molec^{-1}s^{-1}$]	daytime in winter [s^{-1}]	daytime in spring [s^{-1}]	daytime in summer [s^{-1}]
Methanol	$9.00\cdot10^{-13}$ (a		$2.42\cdot10^{-16}$ (f			
Acetaldehyde	$1.50\cdot10^{-12}$ (a		$2.72\cdot10^{-15}$ (g	$1.50\cdot10^{-6}$ (h /$4.4\cdot10^{-6}$(i	$1.42\cdot10^{-6}$(j	$3.27\cdot10^{-6}$ (h
Acetone	$1.80\cdot10^{-13}$ (a		$3.00\cdot10^{-17}$ (g	$2.32\cdot10^{-7}$ (h /$6.51\cdot10^{-8}$(i	$2.10\cdot10^{-8}$(j	$4.85\cdot10^{-7}$ (h
Isoprene	$1.00\cdot10^{-10}$(a	$1.28\cdot10^{-17}$(d	$6.78\cdot10^{-13}$ (d			
Methyl vinyl ketone (MVK)	$3.00\cdot10^{-11}$ (a	$0.47\cdot10^{-17}$(b		$9.40\cdot10^{-7}$(i	$2.91\cdot10^{-7}$(j	
Methyl ethyl ketone (MEK)	$1.20\cdot10^{-12}$ (a	$2.00\cdot10^{-17}$(e		$3.97\cdot10^{-6}$(i	$1.23\cdot10^{-6}$(j	
Benzene	$1.19\cdot10^{-12}$ (a	$1.70\cdot10^{-22}$ (d	$3.00\cdot10^{-17}$ (e			
Methylbutenol (MBO)	$8.83\cdot10^{-12}$ (b	$7.39\cdot10^{-17}$(b				
Toluene	$5.60\cdot10^{-12}$ (a	$4.10\cdot10^{-22}$ (d	$6.79\cdot10^{-17}$ (e			
Hexenal	$3.85\cdot10^{-11}$(b	$9.1\cdot10^{-19}$(d				
Hexanal	$2.82\cdot10^{-11}$(b			$8.84\cdot10^{-6}$(i	$2.74\cdot10^{-6}$(j	
Monoterpenes	$7.50\cdot10^{-11}$ (c	$1.4\cdot10^{-17}$ (c	$7.06\cdot10^{-12}$ (c			

Rate constants (k_{OH}, k_{O3} and k_{NO3}) used in calculations in Tables 2 and 3: a) iupac preferred b) www.chemspider.com (last access: 11:18 17.1.2013). Predicted data are generated using the US Environmental Protection Agency's EPI Suite. c) Monoterpenes' rate constants k_{OH}, k_{O3} and k_{NO3} were calculated as weighted averages of individual monoterpenes typical for SMEAR II (Hakola et al., 2003), individual k-values Atkinson (1994) d) Atkinson (1994) e) http://kinetics.nist.gov/kinetics/Search.jsp (last access: 12:19 17.1.2013) f) Atkinson et al. (1981) g) Rinne

et al. (2007) h) calculated similar to Hellén et al. (2004) i) wintertime photolysis rates scaled from spring-time photolysis rates by radiation j) Hellén et al. (2004)

Table 2. Total atmospheric lifetimes for measured VOCs during day and night at urban background SMEAR III (**paper I**).

VOC	Lifetime on winter day at urban background site	Lifetime on winter night at urban background site	Lifetime on spring day at urban background site	Lifetime on spring night at urban background site
Methanol	234 d	1.1 y	16 d	154 d
Acetaldehyde	22 d[b]	1.0 y	4.4 d	137 d
Acetone	154 d[b]	88 y	32.7 d	34 y
Isoprene	1.00 d	0.7 d	0.1 d	0.4 d
MVK	0.60 d[b]	0.6 d	0.20 d	0.4 d
MEK	0.10 d[b]	0.1 d	0.07 d	0.07 d
Benzene	177 d	69 y	12 d	30 y
MBO	0.30 d	0.3 d	0.1 d	0.2 d
Toluene	38 d	30 y	2.6 d	13 y
Hexenal	4.50 d	21.7 d	0.4 d	16 d
Hexanal	2.70 d[b]	-	0.4 d	-
Monoterpenes	1.00 d	0.2 d	0.2 d	0.06 d

In the calculations the approximated daytime concentrations used for OH and ozone were in winter [OH] = $5.5 \cdot 10^4$ molecules/cm^3 (Hakola et al., 2003) and [O_3] = $4.8 \cdot 10^{11}$ molecules/cm^3 and in spring [OH] = $8.0 \cdot 10^5$ molecules/cm3 (Hakola et al., 2003) and [O_3] = $5.7 \cdot 10^{11}$ molecules/cm^3; the approximated night concentrations used for ozone and NO_3 were in winter [O_3] = $5.7 \cdot 10^{11}$ molecules/cm^3 and scaled [NO_3] = $1.2 \cdot 10^7$ molecules/cm3 (Hakola et al., 2003) and in spring [O_3] = $7.4 \cdot 10^{11}$ molecules/cm3 and scaled [NO_3] = $3.1 \cdot 10^7$ molecules/cm^3 (Hakola et al., 2003). [b] In total life time calculations photolysis rates scaled from global radiation were used.

Table 3. Total atmospheric lifetimes for measured VOCs during day and night at rural SMEAR II (**papers I and II**).

VOC	Lifetime on winter day at rural site	Lifetime on winter night at rural site	Lifetime on spring day at rural site	Lifetime on spring night at rural site	Lifetime on summer day at rural site	Lifetime on summer night at rural site
Methanol	234 d	1.1 y	16 d	154 d	9 d	113 d
Acetaldehyde	7d[a] (22 d)[b]	1 y	4 d	137 d	2 d	101 d
Acetone	48 d[a] (154d)[b]	88 y	33 d	34 y	15 d	25 y
Isoprene	0.8 d	0.7 d	0.1 d	0.3 d		
MVK	0.4 d[b]	0.5 d	0.2 d	0.3 d		
MEK	0.08 d[b]	0.1 d	0.1 d	0.06 d		
Benzene	177 d	66 y	12 d	29 y	6 d	27 y
MBO	0.2 d	0.2 d	0.1 d	0.2 d		
Toluene	38 d	29 y	3 d	13 y	1 d	11 y
Hexenal	4 d	18 d	0.4 d	13 d		
Hexanal	3 d[b]		0.4 d			
Monoterpenes	0.9 d	0.1 d	0.2 d	0.05 d	1 h	0.9 h

In the calculations the approximated concentrations used for OH and ozone were in winter [OH] = $5.5 \cdot 10^4$ molecules/cm^3 (Hakola et al., 2003) and [O^3] = $6.8 \cdot 10^{11}$ molecules/cm^3, in spring [OH] = $8.0 \cdot 10^5$ molecules/cm^3 (Hakola et al., 2003) and [O_3] = $1 \cdot 10^{12}$ molecules/cm3 and in summer [OH] = $1.5 \cdot 10^5$ molecules/cm^3 (Hakola et al., 2003) and [O_3] = $8.6 \cdot 10^{11}$ molecules/cm^3 and approximated night concentrations for ozone and NO_3 were in winter [O_3] = $6.8 \cdot 10^{11}$ molecules/cm^3 and scaled [NO_3] = $1.2 \cdot 10^7$ molecules/cm^3 (Hakola et al., 2003), in spring [O_3] = $9.5 \cdot 10^{11}$ molecules/cm$_3$ and scaled [NO_3] = $3.1 \cdot 10^7$ molecules/cm^3 (Hakola et al., 2003) and in summer [O_3] = $7.1 \cdot 10^{11}$ molecules/cm^3 and scaled [NO_3] = $4.2 \cdot 10^7$ molecules/cm^3 (Hakola et al., 2003). [a)] In total life time calculations photolysis rates calculated similar to Hellén et al. (2004) were used b) In total life time calculations photolysis rates scaled from global radiation were used

At the boreal SMEAR II site, solar radiation changes dramatically from winter to spring/summer: daylight hours increase from approximately 6 hours in winter to 16-18 hours in spring and summer. At SMEAR II the OH radical concentration varies a lot, from approximately 10^4 molecules/cm^3 in winter to 10^5 molecules/cm^3 in spring (Hakola et al., 2003), because the photolysis of ozone is slower in winter than in spring/summer. The total atmospheric lifetime of VOCs thus varies seasonally and diurnally depending on the available radicals, their concentrations and the intensity of solar radiation. The structure of the compounds also affects their reactions with different oxidants or their ability to undergo photolysis, e.g., some OVOCs have photoactive groups (Reimann and Lewis, 2007). In

paper I the total lifetimes of selected VOCs from both biogenic and anthropogenic sources were calculated to define the main oxidants of the VOCs studied in the urban background and the rural boreal forest sites in winter and spring.

During daytime, OH was the primary oxidant for methanol and aromatic compounds in both seasons. The large increase in available OH radicals in spring compared to that in winter had an effect on the daytime total lifetimes, e.g., the daytime lifetime of methanol in winter was 234 days while in spring it was only 16 days. In winter the monoterpenes' lifetime due to OH radicals was about 3 days. Thus in winter the lifetime of monoterpenes was limited by O_3, resulting in a lifetime of 2 days. In spring, however, the lifetime of monoterpenes was limited by OH: the lifetime due to OH was then a few hours, while reactions with O_3 resulted in a lifetime of about 1 day. Although in this case the lifetime of monoterpenes in spring was limited by OH radicals, one should remember that, when studying the different monoterpenes separately, O_3 can still be the primary oxidant for certain of the monoterpenes, e.g., for limonene (Hakola et al., 2012). For the whole OVOC group studied, a single primary oxidant could not be determined; for example acetone and acetaldehyde favour photolysis in both seasons, the main oxidant for methyl ethyl ketone (MEK) was O_3, while hexanal's lifetime was limited by photolysis during winter and by OH during spring. The OVOCs are a group of compounds with differing chemical structures, which explains the several oxidants or degradation by photolysis involved with the OVOC group.

At night-time, the primary oxidant for all the VOCs in this study was NO_3. During the winter night the methanol lifetime was a little over one year; in spring it was about 0.5 year. The lifetimes of aromatic compounds were limited by NO_3, being on a scale of tens of years in both seasons, but their lifetimes were shorter in spring. The lifetime of monoterpenes as limited by NO_3 was 2.5 hours in winter and 1 hour in spring. Comparing the lifetimes of monoterpenes with those of OVOCs and aromatic compounds, it can be seen that terpenes have the shortest lifetimes and are the most reactive group of VOCs studied in this thesis. According to the calculated lifetimes of the VOCs studied, they can be divided into two groups: 1) VOCs with a short lifetime (τ is some hours) and 2) these with a long lifetime (τ >1 day).

4.1.1. VOCs with a short lifetime

VOCs with a short lifetime are usually of biogenic origin such as terpenes. They are known to react quickly with atmospheric oxidants. Due to their reactivity, the BVOCs can participate in several atmospheric processes and are key players in atmospheric chemistry. In this thesis, two aspects of BVOCs were studied: 1) the effects of the production rates of monoterpenes' oxidation products on the nucleation mode particle growth and 2) the influence of BVOCs on the oxidative capacity of the atmosphere.

The oxidation products of monoterpenes are known to include low volatility organic gases, but also other compounds and radicals such as CO, formaldehyde, OH and OH_2 are formed.

The low volatility oxidation products of monoterpenes are observed to participate in new particle formation processes (Tunved et al., 2006), and can affect particle growth processes (Ehn et al., 2014; Laaksonen et al., 2008). These low volatility vapours of oxidation products can condense onto the surfaces of pre-existing particles and thus enhance particle growth, or they can participate directly in the nucleation process (Steiner and Goldstein, 2007). In **paper III**, the production rates of monoterpenes' oxidation products by O_3 and the OH radical were calculated and correlated with the particle growth rates of nucleation mode particles. The oxidation by OH radicals and light intensity are known to be controlling factors for nucleation. However, according to **paper III**, the VMRs of monoterpenes and their oxidation products by O_3 were found to be limiting factors for particle growth in the nucleation mode (7-20 nm). Similar observations have been reported by Hao et al. (2011).

The OH oxidation of BVOCs is a very important loss reaction for VOCs. The oxidation capacity of the boreal forest was therefore studied by measuring the total OH reactivity at SMEAR II (**paper IV)**. The total OH reactivity was measured by the comparative reaction method (CRM), which is described in detail by Sinha et al. (2008). The main results were that there is a missing reactivity, i.e. a difference between the measured and calculated total OH reactivities. The total OH reactivity was calculated based on the measured OH sinks, which in **paper IV** were 30 individual VOCs, CO, NO, NO_2, O_3. In addition to these CH_4, whose concentration was estimated, was also used in the total OH reactivity calculations. Comparing the measured total OH reactivity with that based on the measured trace gases, the ratio of the missing part to the total OH reactivity was observed to be approximately 50 %. In the boreal forest the missing part of the reactivity can probably be accounted for by the presence of unmeasured very reactive biogenic organic compounds such as amines and oxidized compounds (Di Carlo et al., 2004; Sinha et al., 2010; Nölscher et al., 2012, Hellén et al., 2014), which can have an effect on the local atmospheric chemistry.

4.1.2. VOCs with a long life time

Selected OVOCs and aromatic compounds were defined to be long-lived according to their lifetime estimates. Such compounds do not decompose as quickly as terpenes in atmospheric processes, but they still have a role to play in the atmospheric chemistry. However, in this study the purpose was to define potential source areas of selected long-lived VOCs (methanol, acetone, acetaldehyde, benzene and toluene), because long-lived VOCs are also known to be transported over long distances (Ruuskanen et al., 2009) to arrive in Southern Finland. With the help of trajectories, the source areas of VOCs for Southern Finland can be defined from the VOC concentration measurements. The results of the source area analysis are presented in chapter 4.2.3, where the influence of VOC sources is discussed.

4.2. Factors influencing the inter-annual, seasonal and diurnal variations of VOCs

The variation of VOC concentrations has been investigated using both online and offline methods by e.g. Spanke et al. (2001); Hakola et al. (2003, 2012); Hellén et al. (2004); Rinne et al. (2005); Ruuskanen et al. (2009). In the papers included in this thesis, VOCs have been found to have variations between years and seasons as well as diurnally. These variations result from many factors, such as meteorology and mixing, photochemistry and the various different VOC sources. These factors are studied in **papers I**, **II**, **V**. The long-term variations of monoterpenes during years 2000-2007 were investigated in **paper V**. In **paper I**, the seasonal and diurnal variations of VOCs were studied in more detail, especially the transition from winter to spring. The variations of VOCs are also observed to be related to temporary pollution episodes; these were studied during a prescribed forest burning experiment (**paper VI**) and during Russian forest-fire episodes (**paper II**).

4.2.1. Inter-annual, seasonal and diurnal variations

Inter-annual variations of monoterpenes were studied in **paper V**. The measurement period covered the years 2000-2007. The concentrations of several monoterpenes (α-pinene, β-pinene, myrcene, camphene and Δ^3-carene) were observed to increase towards the end of the measurement period in the years 2005-2006 during both winters and summers (**paper V**). The increase in the concentration was lower in the winter than in the summer. At the end of the period in 2007, the winter values decreased back to the same level as they had been at the beginning of the period in 2000. Summer values also decreased somewhat at the end of the period compared to the highest values. The reason for the increased concentrations was not obvious, though a few possible reasons may be mentioned: the measurements were temporarily in another tower and the closest trees grew during the measurements. The effects of meteorological parameters on the concentrations of monoterpenes are discussed in the following chapter 4.2.4. In **paper V** year-to-year variation of monoterpene concentrations was not observed to correlate with temperature. The growth of the trees may explain the increase of α-pinene and Δ^3-carene concentrations. However, the concentration levels of compounds linked to *de novo* biosynthesis (e.g. sabinene and 1, 8-cineol) remained stable. These observations gave an indication that, in addition to vegetation, the elevated concentrations may have been due to some other activities near the site. Forestry operations are known to increase the concentrations and emissions of monoterpenes (Räisänen et al., 2008b; Haapanala et al., 2012, Liao et al., 2011). During the measurement period, the mixed forest area nearby the site was logged and a new measurement hut was also built. However, these events did not match exactly with the times of the increased concentrations. Such occasional and unclear increases in concentrations emphasize the fact that permanent and standardized long-term measurements are needed for VOC concentrations to be reliably monitored.

The seasonal variation of VOCs between winter and spring were studied in **papers I** and **V**. In **paper I** a selection of OVOC, aromatics VOCs and terpenes in two different environments was studied: at the urban background site and at the rural site (Figure 6); in **paper V** a set of monoterpenes was included at the rural site.

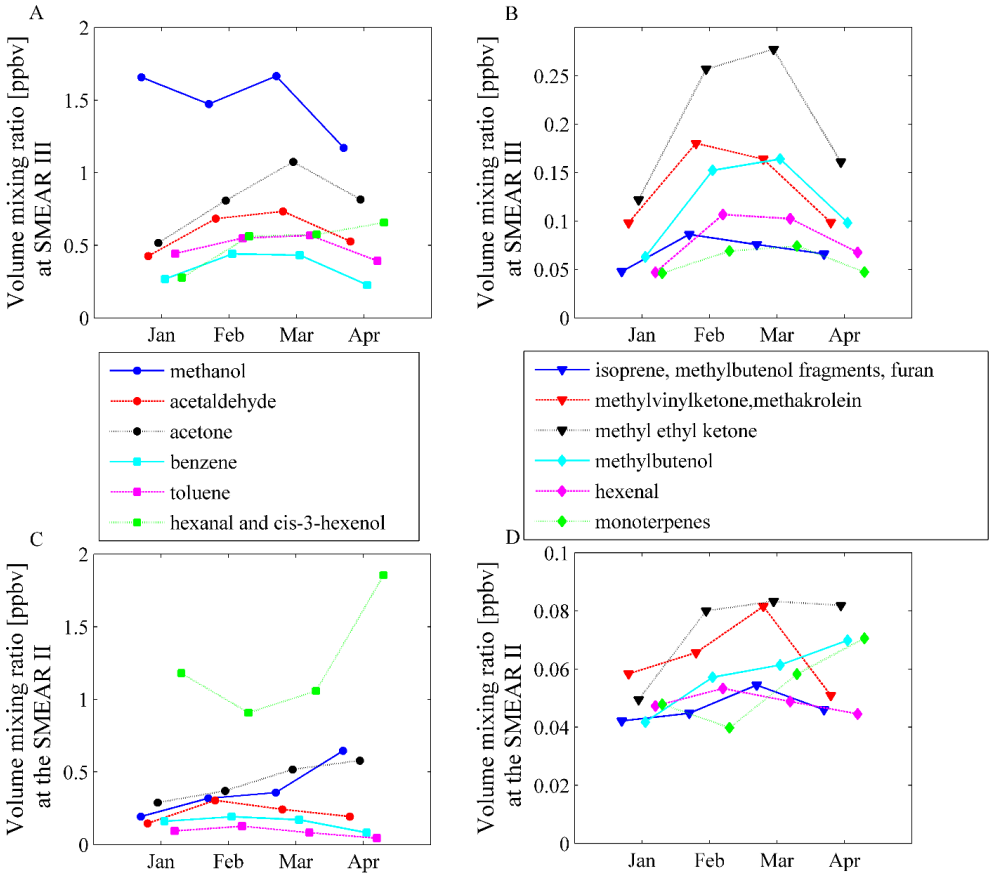

Figure 6. Monthly medians of measured VOCs: methanol (M33), acetaldehyde (M45), acetone (M59), benzene (M79), toluene (M93) and hexanal, cis-3-hexenol (M101), isoprene, methylbutenol fragments, furan (M69), methyl vinyl ketone, methakrolein (M71), methyl ethyl ketone (M73), methylbutenol (M87), hexenal (M99), monoterpenes (137) A) and B) at the urban background SMEAR III station, Helsinki C) and D) at the rural SMEAR II station, Hyytiälä (**paper I**).

The medians of VOC VMRs were mostly higher in the spring and summer than in the winter. This increase of VMRs in spring is probably due to the enhancement of biogenic activity (Hakola et al., 2003). The increases in both the photochemical activity and biogenic emissions were observed have an important effect on the mechanism connecting the biosphere and the atmosphere. New particle formation events were found to be at their highest concurrent with the spring awakening (Dal Maso et al., 2009), while particle growth was at its highest in summer (Kulmala et al., 2004). The VMRs of methanol at the urban site

and of toluene and benzene at both sites were lower in spring than in winter. For AVOCs, the emissions are higher in winter than in spring e.g. due to heating with wood and the cold starts of car engines (Hedberg et al., 2002). An additional explanation for this kind of seasonal behaviour may also be the degradation of compounds due to increased photochemical activity in spring (Rasmusen and Khalil, 1983). The lifetimes of methanol and AVOCs were calculated to decrease in spring due to enhanced photochemistry (**paper I**). There were also some compounds (isoprene, MVK, methacrolein and hexenal) whose concentrations stayed almost constant at the rural site during the transition from winter to spring. This is similar to observations by Ruuskanen et al. (2009). An isoprene concentration maximum is observed to occur during summer from mid-June to mid-September (Hakola et al., 2000, 2003). Isoprene emissions in summer are strongly linked to mature leaves, and thus concentrations stay low outside the growing season (Ruuskanen et al., 2009). MVK and methacrolein are oxidation products of isoprene, and their concentrations at the rural site mainly follow the concentration of isoprene.

In **paper I**, the diurnal variation of four selected VOCs (methanol, benzene, toluene and monoterpenes) was studied in detail. They were selected because of their different reactivity towards atmospheric oxidants (Atkinson, 2000) and their different sources in the atmosphere: methanol is known to originate from both biogenic and anthropogenic sources (Jacob et al., 2005; Singh et al., 2000), benzene and toluene from anthropogenic sources (Singh and Zimmerman, 1992) and monoterpenes mainly from biogenic sources (Jordan et al., 2009; Guenther et al., 1995, 2000). In **paper I** VOCs were observed to have more variation in their diurnal cycles at the urban background site than at the rural site in both seasons. This stronger variation of VOCs in the urban environment compared to that at the rural site is probably due to the presence of many local sources, such as traffic, combustion and industry, at the former. The influence of the different observed VOC sources for urban background and rural sites are studied in a later chapter, 4.2.3. In addition to the different sources, both the photochemical reactivity of compounds and mixing are also observed to have an impact on the shape of the diurnal cycle (Rinne et al., 2005; Hakola et al., 2012). The calculated lifetimes of all the studied VOCs (**paper I**) were shorter in the spring than in the winter due to the fact that photochemical degradation is more efficient in spring than in winter. In Figure 7 mixing time scales (z/u*) are presented for both sites in winter and spring (**paper I**). Mixing was observed to be lower during the winter than during the spring. However, at the urban background site the mixing during the daytime was almost the same in both winter and spring.

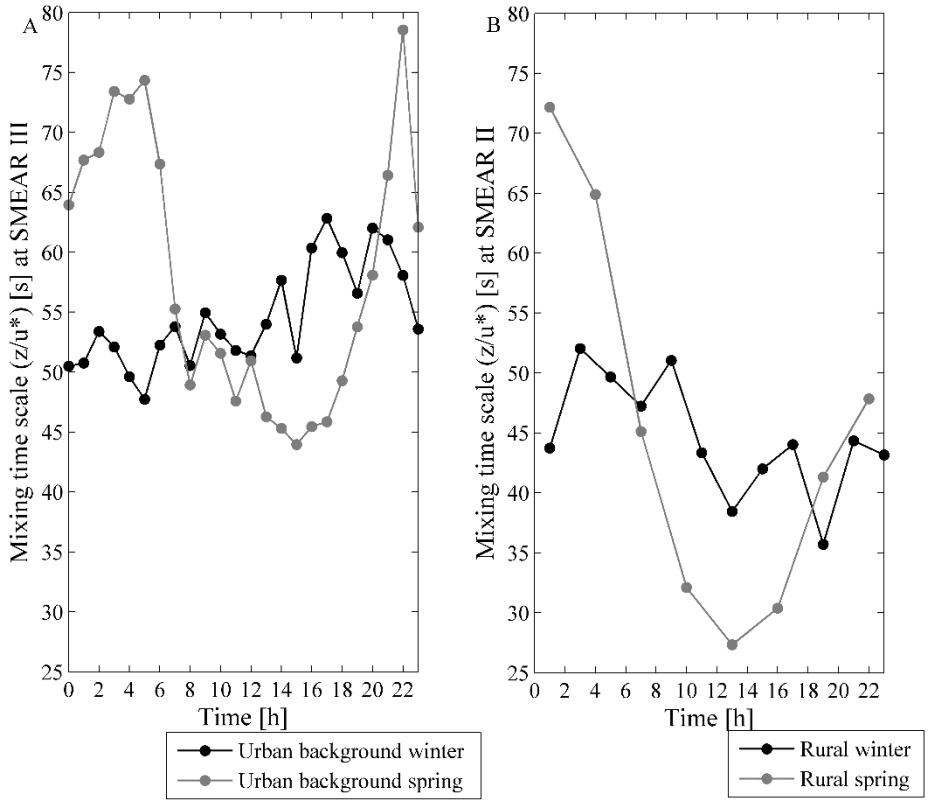

Figure 7. Mixing time scales (z/u*) in winter and in spring A) at the urban background SMEAR III and B) at the rural SMEAR II sites (**paper I**).

Due to this the VMRs of methanol, for example, did not dilute during daytime and stayed nearly constant at the urban background site in both seasons (Figure 8 A). The diurnal pattern for monoterpenes differed in winter at both sites and in spring at the urban site from the diurnal pattern that is observed in the coniferous forest for biogenic emissions. In the rural spring, the VMR maxima of monoterpenes were observed in the late evening and early morning (Figure 9D). At the rural site the mixing was observed to be more pronounced in the spring than in the winter (Figure 7 B). Strong mixing dilutes the monoterpenes and thus, in combination with enhanced photochemical degradation reactions, lowers their daytime VMRs (Figure 9 D). At the rural site the diurnal cycle of monoterpenes in spring thus followed a similar pattern found for the biogenic monoterpenes in previous studies by, e.g., Rinne et al. (2007); Ruuskanen et al. (2009); Hakola et al. (2012).

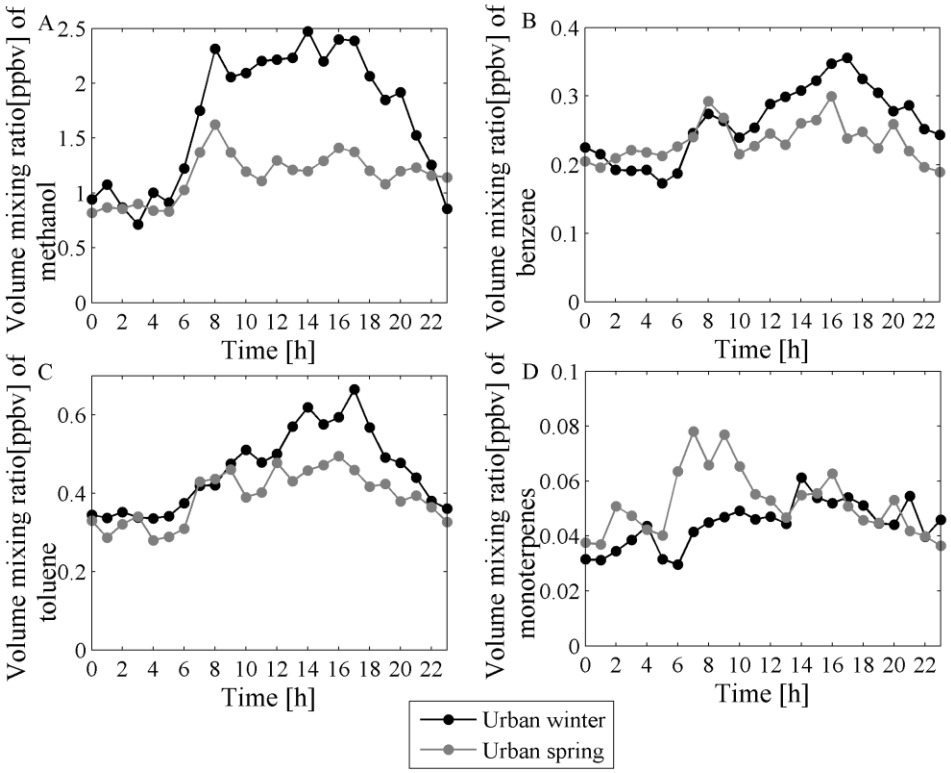

Figure 8. Median diurnal cycles of selected VOCs A) methanol (M 33) B) benzene (M 79) C) toluene (M93) and D) monoterpenes (M137) at the urban background SMEAR III station, Helsinki (**paper I**).

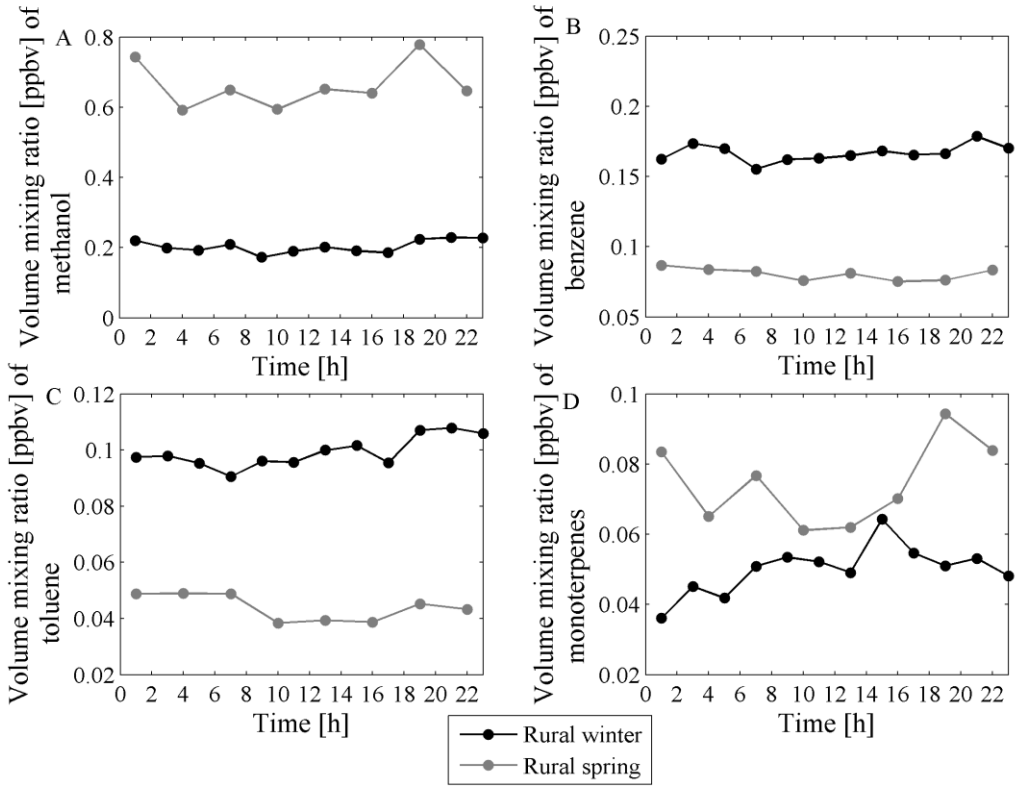

Figure 9. Median diurnal cycles of selected VOCs A) methanol (M 33) B) benzene (M 79) C) toluene (M93) and D) monoterpenes (M137) at the rural SMEAR II station, Hyytiälä (**paper I**).

4.2.2.Meteorological parameters

The influence of several meteorological parameters (temperature, radiation, rainfall, and wind speed and direction) was studied in **paper V** in an attempt to find an explanation for the observed increase in VOC concentrations over the measurement period (2000-2007). In previous studies, e.g., Hakola et al. (2003), temperature was observed to be one of the most important factors affecting monoterpene concentrations. The monoterpene concentration maximum was observed during summer (June-August) (Hakola et al., 2003, 2006). However, the connection between temperature and concentrations of monoterpenes is complex. Maximum emissions of monoterpenes are observed when the temperature is high. However, at the same time the loss reactions of monoterpenes are at their fastest, and also the top of the boundary layer is usually at its highest. These facts support the argument that the dilution effect is then strong. Although some correlations between temperature and monoterpene concentrations were observed in **paper V**, temperature alone was not considered to explain the increase in monoterpenes concentrations.

The transport of monoterpenes from neighbouring areas was also studied by correlating the concentrations of monoterpenes with wind speed and direction. However, in **paper V** no correlations were found and thus the possible effect of near-by local sources such as saw-mills, in inducing the elevated concentrations could not be recognized. However, in later studies, high concentrations of monoterpenes were found to be linked to the near-by village of Korkeakoski, where a large saw-mill is located (e.g. Liao et al., 2011).

Schade et al. (1999) and Helmig et al. (1998) observed an increase in monoterpene concentrations related to rain events. However, in **paper V** the concentrations of monoterpenes during the two rainiest summers were observed to vary a lot. Significant correlations between rainfall and concentrations of monoterpenes were not found. Unfortunately, the relationship between rainfall and concentrations is probably biased, because samples were not taken during heavy rain.

Thus, based on **paper V**, the increase in monoterpene concentrations during the period of measurements was not possible to explain by the meteorological parameters studied.

4.2.3. Main sources and source areas contributing to VOC variations

The receptor model Unmix gave various different sources for VOCs (Figure 10). The sources (Traffic, Distant, Methanol, Acetone, Biogenic I and II, Regional, Accumulation-mode-particle and Monoterpenes) were identified based on the source compositions and the variations of the source contributions (**paper I**). For example, the Unmix source called Traffic included aromatic compounds, OVOCs, some terpenes and at the rural site also NO_x and CO. The diurnal pattern of the traffic source also varied more than e.g. the diurnal pattern of the Distant source, the former making its highest contribution during afternoon rush hours at the urban site. Two biogenic sources: Biogenic I and II included different compounds. The main compounds of Biogenic I were terpenes and of Biogenic II was methanol. The diurnal cycle of Biogenic I was similar to the diurnal pattern of monoterpenes in spring which indicated that Biogenic I emissions may be more local that emissions of Biogenic II. The sources given by Unmix have been denoted with a capital letter in this thesis to avoid confusion with the sources as real world phenomena.

At both sites Traffic and Distant sources were always present. In addition to these, Methanol and Acetone sources were found in winter and Biogenic I and II in spring at the urban background site. At the rural site, additional sources to Distant and Traffic were the Regional, Accumulation-mode-particle and Monoterpene sources.

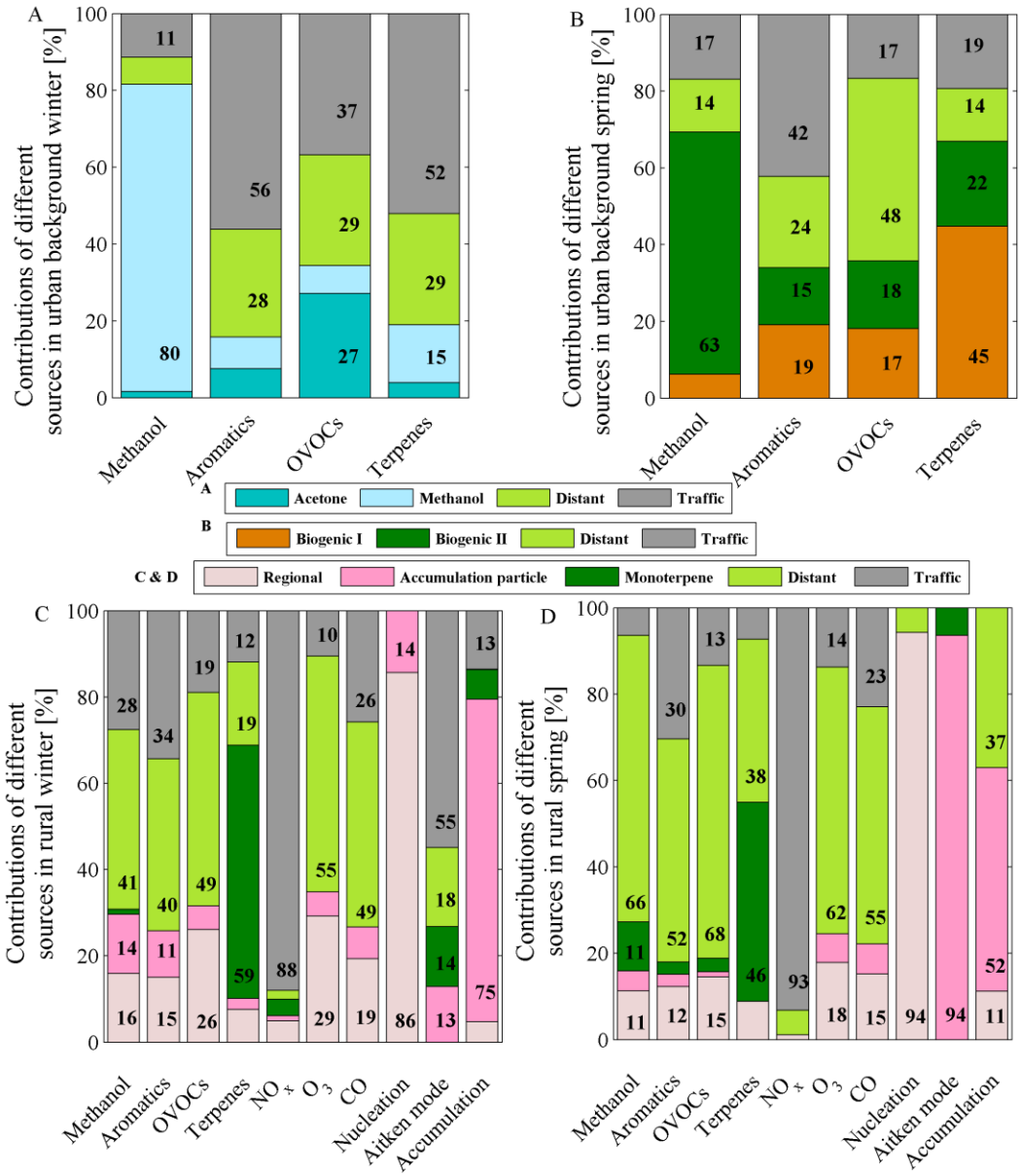

Figure 10. Contributions of different UM-sources to measured species A) urban background winter B) urban background spring C) rural winter D) rural spring. Aromatics included benzene and toluene; OVOCs: acetone, acetaldehyde, MVK, MEK, MBO, hexanal and hexenal; terpenes: isoprene and monoterpenes. Nucleation mode included particles smaller than 25 nm, Aitken mode particles 25-100 nm and accumulation mode larger than 100 nm. If the contribution of group was lower than 10% the percentage has not been marked on the bars (**paper I**).

The influence of the various sources on VOC diurnal variations is described in detail. As stated earlier, compared to aromatic compounds and monoterpenes methanol has several sources. This can also be seen from methanol's diurnal pattern. At the urban background site it has a clear diurnal variation, but at the rural site the diurnal cycle was almost non-existent in both winter and spring. This suggested that methanol had different sources at these two sites. In an urban environment, methanol has been observed to have several anthropogenic sources, such as traffic and evaporation related to the cold starts of car engines (Hellén et al., 2012; Hu et al., 2007), as well as solvents and industrial sources (Jacob et al., 2005), while in rural and remote environments it is mostly related to biogenic emissions (Janson and de Serves, 2001; Rinne et al., 2007, 2009; Fall, 2003; Jacob et al., 2002, 2005; Singh et al., 1994). In winter methanol VMRs were explained mainly by one source of its own (Methanol, 80%, **paper I**), which depicts the fact that it has multiple sources. In the spring an enhanced biogenic influence (63%) was observed in the source analysis at the urban site. Although the mixing was observed to be at the same level in both seasons, the diurnal cycle of methanol at the urban background site was still found to be stronger in the winter than in the spring. The higher VMRs of methanol in winter were probably due to a shallower boundary layer and slower photochemical degradation reactions then. At the rural site, the low level of variation in the methanol diurnal cycle is due to the large contribution from the distant source (41%) and thus long-term transportation during winter. Although the distant source (66%) also dominated in the rural spring, the slightly enhanced diurnal cycle and an increase in the VMR level in that season (Figure 9 A) indicate the effect of biogenic (11%) and regional photochemical (11%) sources. The absence of a proper diurnal cycle may indicate that there is a balance between sources and sinks (Bader et al., 2014).

The observed diurnal variations of aromatic compounds at the urban background site followed quite well the diurnal cycle of traffic counts (**paper I**). Traffic also proved to be the main source of aromatic compounds in the source analysis (56%/ 42%) in both seasons at the urban background site. At the rural site in winter, the Traffic (34 %) and Distant (40%) sources were almost equal sources for aromatic compounds. However, in spring, due to enhanced mixing, the contribution of the local Traffic (30%) source was lower than that of the Distant source (52%). In addition to this, the effects of increased photochemical degradation reactions were clearly visible in the case of the diurnal cycles of aromatic compounds in spring. Thus the VMRs of aromatic compounds were clearly lower in spring than in winter at the rural site (Figure 9 B, C).

In several studies (e.g. de Gouw et al., 2005; Gelencsér et al., 1997; Kourditis et al., 2002; Barrefors, 1996) the toluene to benzene ratio was used as an indicator of the age of air masses. In Helsinki, the toluene-to-benzene ratio followed to some extent traffic rates, rising when the emission was fresh and declining when it was mixed into the surrounding air. The median toluene-to-benzene ratio varied from 1.64 to 1.74 (**paper I**). These values were lower than the ratios observed earlier by e.g. Barrefors, (1996) in Sweden or Kourtidis et al., (2002) in Greece. Hellén et al. (2006) found the main sources of aromatic hydrocarbons in Helsinki

to have been traffic and wood combustion, which agrees well with the observations of this study. Wood combustion is known to reduce the toluene-to-benzene ratio (Hedberg et al., 2002; Hellén et al., 2006), but also the number of cars and the different fuels used in cars have an effect on the ratio. At the rural site the diurnal pattern of toluene-to-benzene ratios had no variation. The median values of the ratios were 0.6 and 0.55 in winter and spring, and were thus lower than the ratios observed at the urban background site (**paper I**). These observations support the fact that the local sources e.g. traffic were more important at the urban background site than at the rural site.

The diurnal cycles of monoterpenes at the rural site were observed to have clearly different shapes during winter and spring (**paper I**). In the winter, the shape of the monoterpenes' diurnal pattern was, at both sites, influenced by anthropogenic sources. This also fitted well with the results of the source analysis. At the urban background site, terpenes were explained by Traffic (winter 52%/ spring 19%). In earlier studies (Borbon et al., 2001; Hellén et al., 2006, 2012) terpenes were related to anthropogenic emissions such as traffic and wood combustion. Thus, it is also possible that some other emissions (e.g. wood combustion) were not properly separated from the Traffic source by Unmix in **paper I**. In the spring the increase in biogenic influences was observed at both sites. Source analysis also agreed with the enhancement of the biogenic source in spring. At the urban site, Biogenic source I (45%) was the main source of monoterpenes in spring. Similar to the urban background site, monoterpenes at the rural site had an anthropogenic source (59 %) in winter, while in spring the biogenic source (46%) was dominant.

Long-range transport has been observed to be an important source especially for long-lived VOCs (Hellén et al., 2006; Ruuskanen et al., 2009). In **paper II** the source areas for VOCs with a long lifetime (methanol, acetonitrile, acetaldehyde, acetone, benzene and toluene) were analyzed. The source areas (Figure 11) having the most remarkable effect on the measured high VMRs at SMEAR II were observed to be located in Eastern Europe including Western Russia. Northern Fennoscandia seemed to be quite free of anthropogenic sources of VOCs. Thus the VMRs of VOCs in air masses arriving from a northern direction were low.

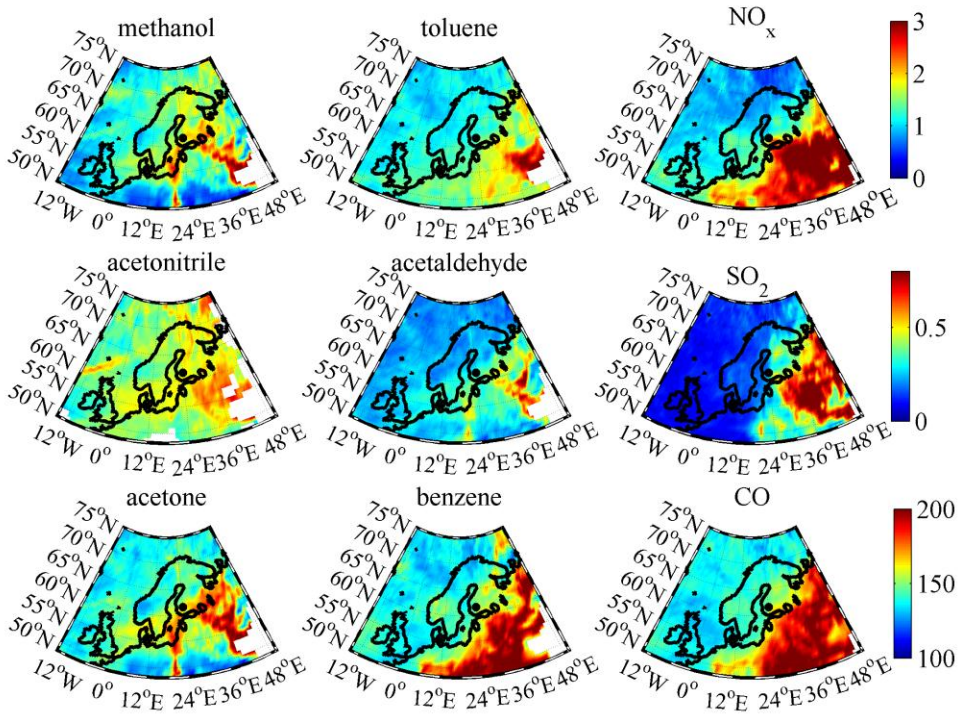

Figure 11. Mean trajectory fields (2006-2011) of selected VOCs and trace gases [ppb_v]. VMR scales are presented on the right, with the scale for each compound being further multiplied in the case of each compound by the indicated factor 10, 100 or 1000 if needed. Topmost row: methanol, toluene (multiplied by 10) and nitrogen oxides (NO_x). Middle row: acetonitrile (multiplied by 10), acetaldehyde, sulphur dioxide (SO_2). Bottom row: acetone (multiplied by 100), benzene (multiplied by 1000) and carbon monoxide (CO). The SMEAR II site is marked by a dot on the maps (**paper II**).

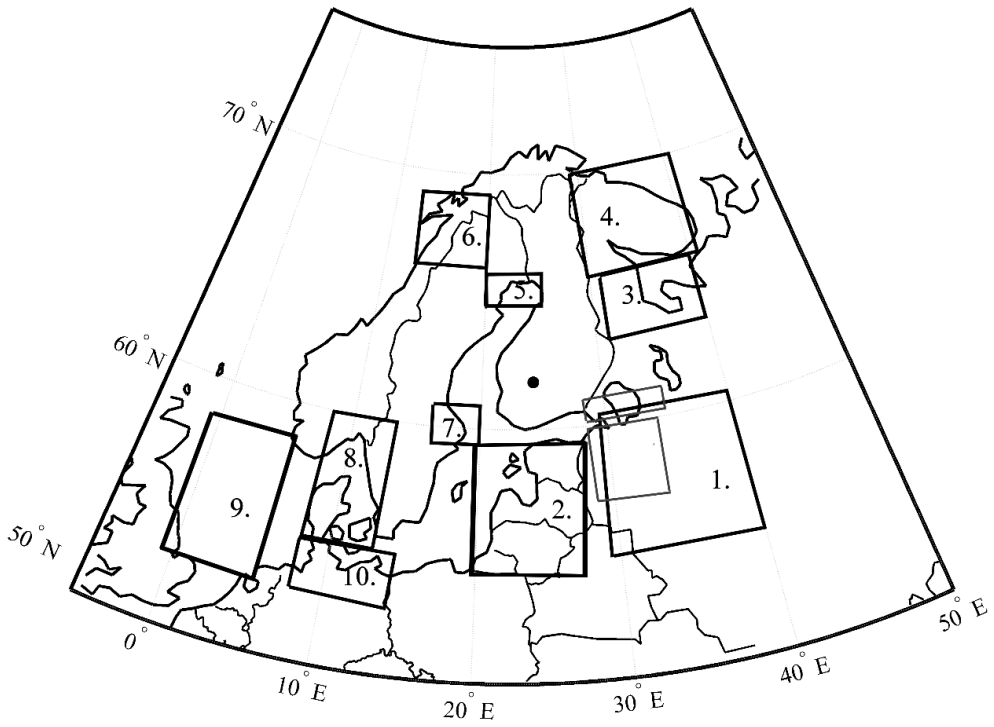

Figure 12. Source areas of VOCs selected for the analysis: 1) Western Russia 2) Northern Poland, Kaliningrad and Baltic countries 3) Karelia and the White Sea 4) Kola Peninsula and Barents Sea 5) Bay of Bothnia 6) Coast of Norwegian Sea and Northern Sweden 7) Stockholm area 8) Skagerrak 9) North Sea and coastal areas 10) Northern Germany. Two forest fire source areas, limited in time, are marked by grey boxes. These are treated separately for the episodes (see chapter 4.2.4). The SMEAR II site is marked by a dot on the map (**paper II**).

VOC source areas were studied in detail separately during winter and summer by selecting ten source areas (Figure 12). To evaluate the source areas for the studied VOCs, two different VMR trajectory fields were calculated: 1) the momentary VOC VMR trajectory field from the measured one-hour median values and 2) the interpolated VOC VMR trajectory field from a linear interpolation of the monthly median values corresponding to the same time period. A differential source field was calculated by subtracting the latter from the momentary field. The average values of the differential source field for the ten areas listed above are presented in Figure 13.

From Figure 13 it can be seen that main source areas for almost all VOCs are located in Eastern Europe. In addition to these source areas that were common to most of the studied compounds, the study showed that all compounds have specific source areas of their own. As noted earlier from observations in this study, methanol is a very abundant VOC in the atmosphere, with both biogenic and anthropogenic sources (Jacob et al., 2005). Nearly all of

the selected areas were sources of methanol. Eastern Europe was observed to be an important emitter of OVOCs (methanol, acetaldehyde and acetone) in general (**paper II**). Earlier, Eastern Europe has been reported to be an important emitter of carbonyls (Hellén et al., 2004) In addition to these source areas, acetone and acetaldehyde also arrived from the areas of Stockholm, the Skagerrak, the North Sea and its coastal areas and Northern Germany. All these areas are known to have traffic emissions and solvent use related to various industries.

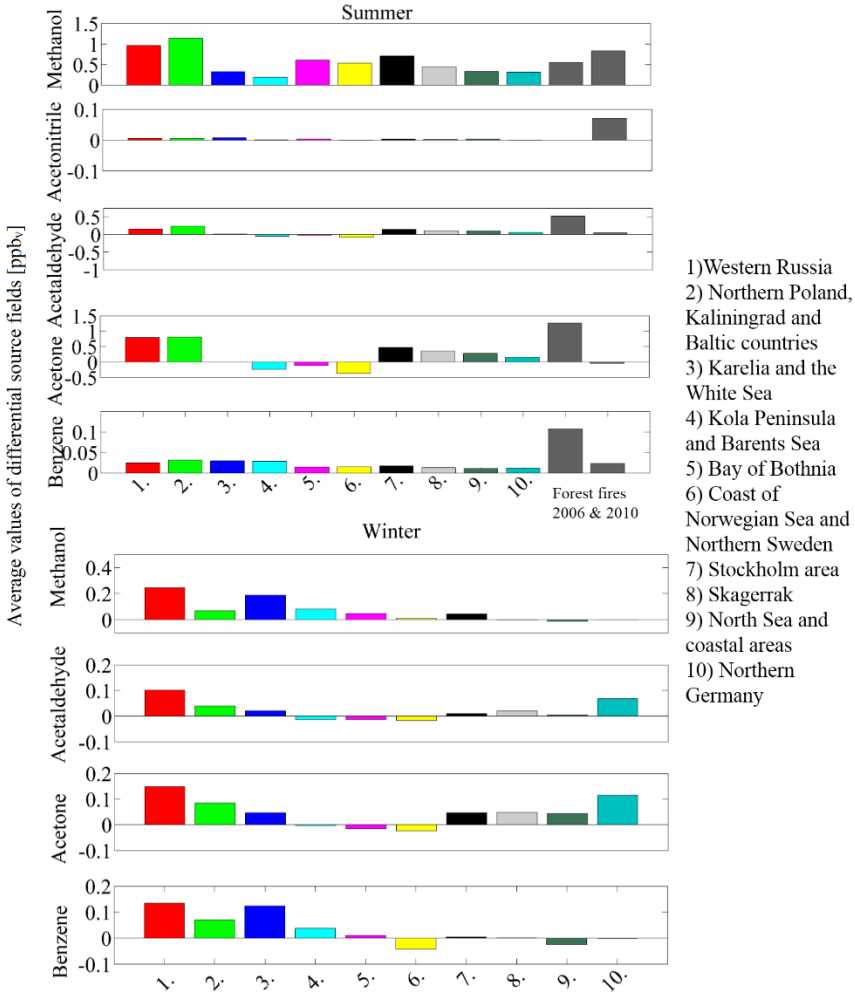

Figure 13. Average values of differential source fields during summer (upper panel) and during winter (lower panel) for methanol (m 33), (acetonitrile (m 42), in summer only), acetaldehyde (m 45), acetone (m 59) and benzene (m 79) (figure axis modified from **paper II**).The differential source field was calculated by subtracting the interpolated source area values from the directly-measured source areas values.

Primary biogenic emissions and the oxidation of hydrocarbons are recognized to be the main global sources of acetaldehyde (Singh et al., 2004). Acetaldehyde's relatively short

summertime lifetime (2 days) can add some uncertainty to the source area analysis for this compound. Benzene was also found to have sources in the area of the Kola Peninsula related to the petrochemical industry and mining. However, in this study the active oil and gas extraction area of the North Sea did not act as a distinguishable source area for aromatic VOCs. Eastern European forest fires were also separated into their own source areas for VOCs. These are discussed in detail in the next chapter, 4.2.4. Source areas appeared to have predominantly anthropogenic emissions and most of them (eight out of ten) were located in an easterly or southerly direction from Finland. However, based on trajectory and Unmix receptor analysis, Eastern Europe including Western Russia seemed to be the most important source to influence the highest VMRs of VOCs. The impact of Western Europe on VOCs emissions has clearly decreased. Due to European Union regulations, the total VOC emissions from that area have decreased by about 60% since 1990 (EMEP, 2012).

Northern Europe comprises a large boreal forest zone, which is a significant emitter of short-lived BVOCs, e.g., terpenoids. Their concentrations are relatively low due to their high atmospheric reactivity (Hakola et al., 2003) compared to long-lived VOCs. Thus, the forest areas were not distinguishable as distinct source areas but probably contributed to background levels. During summertime minor source areas were detected in the Baltic Sea; these should not be of anthropogenic origin, but could have been the result of, for example, algae or cyanobacteria.

4.2.4.Forest fires causing occasional pollution plumes

Earlier in this thesis it was stated that the VOCs were found to have both biogenic and anthropogenic sources that were the cause of variations in VOC VMRs. Variations originating from traffic and biogenic emissions are more predictable than sudden pollution plumes, e.g., forest fires. These pollution episodes can be used to estimate the ability of the trajectory analysis to identify source areas. Biomass burning has previously been observed to be a source of VOCs in several field and laboratory studies (e.g. Crutzen and Andreae, 1990; Holzinger et al., 1999; de Gouw et al., 2006). Hydrocarbons released from fires are photochemically active, and thus ozone and NO_x formation related to fire episodes has been reported (e.g. Crutzen and Andreae, 1990; Wofsy et al., 1992; Mauzerall et al., 1998; Goode et al., 2000; McKeen et al., 2002). Acetonitrile is a well-known marker compound for emissions from biomass burning (de Gouw et al., 2003; 2006; Holzinger et al., 1999; Simpson et al., 2011). Also the OVOCs, aromatic VOCs (benzene and toluene) and furans have been connected with biomass burning in different studies (Koppmann and Wildt, 2007; de Gouw et al., 2006). In **paper II** two particularly active forest fire episodes, with several hotspots, were studied. These occurred in Russia in the summers of 2006 and 2010 and also had an influence on the air quality in Finland (Leino et al., 2014). The forest fire periods and locations are described in detail in **paper II**. In **paper II** the forest fire locations and acetonitrile's mean VMR field from trajectory analysis have been compared. One can clearly

see that acetonitrile is originating from the burning area. Mean VMR values of methanol, acetonitrile, benzene, SO_2 and CO were also calculated for periods both before and during the forest fire episodes in both years. In 2010 acetonitrile was observed to increase from 0.06 ppb_v to 0.13 ppb_v. In 2006 (2010), the mean VMR values of benzene increased from 0.05 ppb_v (0.08 ppb_v) to 0.09 ppb_v (0.17 ppb_v). Similarly elevated concentrations were observed for CO in air masses associated with forest fires. In **paper VI** the various factors related to a one-day experiment involving the prescribed burning of logging slash at SMEAR II in summer 2009 were studied. A detailed description of the measurements included in the experiment is given in **paper VI**. Carbon monoxide (CO) was used as a burning marker. Several VOC concentrations (acetonitrile, dimethyl furan, methanol and benzene) were observed to follow the CO trends.

5. Authors contribution and review of the papers

I was responsible for writing this introduction. In **paper I** I was responsible for the data analysis and most of the writing. In **paper II** I have participated in measurements starting from year the 2008, have been occasionally responsible from measurements, and was responsible for the data analysis and most of the writing. In **paper III** I was responsible for calculating production rates of monoterpenes oxidation products and commenting on the manuscript. In **paper IV** I was responsible for taking adsorption samples during measurements and commenting on the manuscript. In the case of **paper V** I was responsible for supplying the meteorological data from the SMEAR II data base and combining it with the measured VOC data; I also studied the possible connection between the observed concentration of monoterpenes and the meteorological parameters (wind direction and speed) and commented on the manuscript. In **paper VI** I was responsible for the planning of measurements and installing the PTR-MS measurements; I was also responsible for the data analysis of the PTR-MS data and for commenting on the manuscript.

In **paper I** the diurnal and seasonal variations of selected VOCs from biogenic and anthropogenic sources were studied at the urban background, SMEAR III station and the rural, SMEAR II station in winter and spring. The lifetimes and primary oxidants of VOCs studied were estimated for both seasons. The main sources for both sites were determined using the Unmix 6.0 multivariate receptor model. VOC VMRs were mainly higher and also had more variation at the urban background site than at the rural site. The biogenic influence was enhanced in spring. The effect of long-distance transport on the observed VMRs was found at the both sites.

In **paper II** the source areas of long-lived VOCs were studied using long term trace gas concentration measurements during the years, 2006-2011 making use of HYSPLIT four-day backward trajectories. During the measurement period, two different forest fires episodes occurred (in 2006 and 2010) which were used to confirm the reliability of the trajectory analysis. The source profiles of the trace gases were studied by receptor analysis. Based on trajectory and source analyses, the highest VMRs originate from eastern and southern continental Europe. The forest fire episodes appeared to increase the VMRs of certain trace gases.

In **paper III** a study was made of the variation of the growth rates of nucleation mode particles. Particle growth rates were estimated using particle size distribution measurements. Particle size distribution was measured with three different instruments. In analysis also two different growth rate analysis methods were tested. The large set of ambient meteorological parameters and trace gas concentrations were studied together with particle growth rates to study the limiting factors for aerosol growth. Related to this thesis, it was found that the

VMRs of monoterpenes and the production rates of monoterpene oxidation products were correlated with the growth rates of nucleation mode particles. The VMRs of the precursor gases and their oxidation products were observed to have an impact on the particle growth of nucleation mode particles.

In paper IV, the oxidative capacity of the boreal forest environment was estimated by measuring the total OH reactivity with the comparative reaction method during a short campaign at SMEAR II in August 2008. The measured total OH reactivity was compared with the calculated OH reactivity, and the missing OH reactivity was thus determined. The missing OH reactivity observed in this study was due to unmeasured reactive organic compounds.

Paper V presents long-term measurements (2000-2007) of monoterpene concentrations at the rural boreal SMEAR II site. Monoterpenes were observed to have seasonal and annual variations. Over the period of the measurements, both the summer and winter concentrations of some monoterpenes increased. The reasons for these increases in the concentrations were studied with respect to various meteorological parameters, but these could not explain the observed increases. Human activities near the site were therefore assumed to cause the higher concentrations.

Paper VI presents the results of a prescribed biomass burning experiment conducted at Hyytiälä in June 2009. Aerosol and trace gas emissions from fires of slash fuels, and the effect of fire on soil properties were studied in a controlled environment. The purpose of the prescribed experiment was to get an increased knowledge of the estimated burned biomass, the meteorological conditions during the experiment, the characterization of the aerosols and gases emitted and the observed dispersion of aerosols. Related to this thesis, ambient VOC VMRs related to biomass burning (e.g. acetonitrile, furan and aromatic compounds) were studied. These were found to have higher VMRs simultaneously with the observed carbon monoxide peaks.

6. Conclusions

The variations in the concentrations as changes in the volume mixing ratios of volatile organic compounds due to different sources and source areas were studied in Southern Finland. The influences of transport and transformation on the VMRs of VOCs and aerosol growth were also analyzed. The VOC VMRs were measured at two different locations: the rural SMEAR II site at Hyytiälä and the urban background SMEAR III site, in Helsinki. The VMRs of almost all VOCs (except monoterpenes and hexanal) were observed to be higher and to show more variation in their diurnal cycles at the urban background site than at the rural site. This was probably due to the variety of local sources affecting the urban background site. At the rural site, the amount of monoterpenes was found to increase towards the end of the measurements (years 2005-2007). Human activities near the rural site and in neighbouring areas were proposed to be the most probable explanation for these inter-annual variations of monoterpenes at SMEAR II.

During winter the anthropogenic influence dominated VOC volume mixing ratios at both sites. Even monoterpenes were found to originate from anthropogenic sources in winter. In the spring, biogenic activity increased and the VMRs of most of the compounds were higher in spring than in winter. The lower VMRs of anthropogenic compounds in the spring were due to less emission from sources such as wood combustion and also to springtime enhanced photochemical loss reactions. The diurnal variation of the VMR of monoterpenes was observed to vary between winter and spring due to the anthropogenic influence in winter. This behaviour indicated the change of sources between the seasons. Mixing and thus the dilution effect on locally-emitted VOCs VMRs was also observed to increase in spring. The dilution effect, combined with enhanced photochemical loss reactions, resulted in low daytime VMRs observed, for example, in the diurnal pattern of short-lived monoterpenes. The receptor analysis also supported the presence of anthropogenic sources in winter and the increase in biogenic activity in spring. At the urban site, traffic was the main source of aromatics in both seasons; OVOCs and monoterpenes in winter. In the spring the biogenic activity related to monoterpenes and the share of transported OVOCs were augmented. Similarly, at the rural site traffic was responsible for a part of the VMRs of aromatic compounds and OVOCs, but their VMRs were also explained by distant and regional sources.

As long-distance transport was found to be important source of long-lived VOCs in Southern Finland, their source areas could be studied with trajectories. The measurement period included two forest fire pollution events in Eastern Europe and a one-day prescribed burning experiment conducted near SMEAR II. All three episodes were observed to increase the VMRs of VOCs related to biomass burning (acetonitrile and aromatic compounds). The forest fire pollution events were well captured by the trajectory analysis which showed the analysis methods were working. Trajectory analysis revealed that the major part of long-lived VOCs and their high VMRs had their origin in air masses from source areas in Eastern

Europe including Western Russia. The northern area was almost free of VOC sources and thus the air masses arriving from a northerly direction were characterized by lower VMRs of the VOCs studied. The selected source areas seemed to have increased emissions due to anthropogenic activity: they were mainly located in areas with a lot of industry. All of the VOCs studied seemed to have their own specific source areas e.g. benzene came from areas related to the petrochemical industry and OVOCs from areas where solvents are used in industry. However, Eastern Europe was still the most prolific source area for all VOCs.

Consistent with the shorter lifetimes of the BVOCs compared to OVOCs, the former were observed to be more reactive than the long-lived VOCs. The influence of atmospheric chemistry on VOCs was thus studied with BVOCs. The effects of the oxidation products of monoterpenes on nucleation mode particle growth were studied. Monoterpenes and their oxidation products by ozone were observed to have a role as limiting factors on particle growth. The photochemical activity and importance of OH radicals as a daytime oxidant for VOCs were observed to increase in the spring. The influence of VOCs on the OH oxidative capacity of the atmosphere was estimated by measuring the total OH reactivity in a boreal forest during the short campaign in summer 2008. A missing OH reactivity, probably due to unmeasured VOCs, was observed. There exists thus an unknown amount of reactive organic compounds that may have effects on atmospheric processes, e.g., aerosol growth.

In the future it is important to continue monitoring VOC concentrations with permanent and standardized online measurements so that long-term trends can be defined. Knowing the trends of VOCs, their impact on air quality can be better evaluated and, for example, the effects of the use of biofuels on ambient VOC VMRs can be determined. Measurements of the VMRs of VOCs and especially those of BVOCs are needed in studies of aerosol formation and climate change. Similarly, the budget of unmeasured reactive compounds is important to determine so that air quality, aerosol formation and growth models can be improved, and also to correct our knowledge of the oxidative capacity of atmosphere.

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